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The Synthesis of Guanidine from Urea (Part 3)

E. Roberts and J. V. Griffiths

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EXPLOSIVES RESEARCH AND DEVELOPMENT ESTABLISHMENT

E.R.D.E. REPORT NO. 41/R/49

The Synthesis of Guanidine from Urea

(Part 3)

by

Elwyn Roberts and John Vernon Griffiths

This report does not contain information of overseas origin

Submitted by.....A Forster.....
A. FORSTER S.E.I.

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Contents

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References

Departmental File No. XR.441/61

Other papers:

Departmental File No. C.R. Temp. 7/32/3/1 (E.R.D.E. Report No. 7/R/49 (Part 1)).

Departmental File No. XR.441/56 (E.R.D.E. Report No. 22/R/49 (Part 2)).

Departmental File No. XR.130/24 (Patent Application 8979/49).

Departmental File No. XR.130/53 (Patent Application 16762/49).

Departmental File No. XR.130/42 (Patent Application 16880/49).

Departmental File No. XR.130/54 (Patent Application 18892/49).

Abstract

1. Object of Investigation

To develop a process for the production of nitroguanidine (picrite) based on urea.

2. Scope of Investigation

The formation of O-ethyl-isourea, by condensation of urea and diethyl sulphate under anhydrous conditions and in absence of solvent, has been studied varying the molar ratio, urea : diethyl sulphate, temperature of alkylation and time of reaction. The rate and extent of formation of O-ethyl-isourea was followed indirectly by its conversion to guanidine by amination.

The effect of ethylating urea in the presence of a base, e.g. pyridine, has been investigated.

The heat of reaction between urea and diethyl sulphate has been assessed in a preliminary manner.

The alkylation of urea using di-isopropyl sulphate, ethylene and isobutylene has been studied under neutral and acid conditions.

The direct amination, using gaseous ammonia, of the product of ethylation of urea, O-ethyl-isourea ethyl hydrogen sulphate, to give guanidinium ethyl sulphate and alcohol has been studied.

An attempt has been made, by action of heat, to convert guanidinium ethyl sulphate directly to guanidine sulphate and diethyl sulphate.

The acid hydrolysis of guanidinium ethyl sulphate to give guanidinium hydrogen sulphate and alcohol has been studied using varying acid concentrations. The stability to heat of a solution of guanidinium hydrogen sulphate in concentrated sulphuric acid has been examined.

The nitration of guanidinium hydrogen sulphate has been studied varying the molar ratio, guanidine : H_2SO_4 : HNO_3, the temperature and time of nitration. The purity of the product, nitroguanidine (picrite), has been examined.

3. Conclusions

The formation of O-ethyl-isourea is optimum, ca. 72-73 per cent, using the molar ratio, urea : diethyl sulphate, 1 : 1 after 1 hour at 100°C., 30 mins. 110°C., or 15-20 mins. at 120°C. The addition of a base, pyridine, has no effect on the yield. The heat of reaction is of a low order.

The maximum yield of guanidine, based on urea, using di-isopropyl sulphate was 48 per cent. Di-isopropyl sulphate is intrinsically unstable.

Ethylene and isobutylene do not alkylate urea under the conditions investigated.

The amination of O-ethyl-isourea ethyl hydrogen sulphate proceeds rapidly and quantitatively to give guanidinium ethyl sulphate under the conditions investigated, the alcohol liberated being equivalent to the guanidine formed. The direct conversion of guanidinium ethyl sulphate to guanidine sulphate and diethyl sulphate was not possible.

The conversion of guanidinium ethyl sulphate to guanidinium hydrogen sulphate and alcohol by acid hydrolysis is rapid and quantitative. Solutions of guanidinium hydrogen sulphate in concentrated sulphuric acid are stable at elevated temperatures.

The conversion of guanidinium hydrogen sulphate to nitroguanidine (picrite) is optimum, ca. 90 per cent, using the molar ratio, guanidine : H_2SO_4 : HNO_3, 1.0 : 3.74 : 1.4 and nitrating at 10°C. for 30 mins. The recrystallised product satisfies service specification tests for picrite.

On the basis of the studies respecting the stages of alkylation, amination, hydrolysis and nitration the elements of a process for the production of nitroguanidine (picrite) from urea have been established. The yield, based on urea, of nitroguanidine, of satisfactory purity, is 63 per cent which compares favourably with that obtained, viz. 54 per cent based on nitrolim, in the Welland process.

4. Recommendations

It is recommended, that:

(i) A more critical examination be made of each stage in the proposed process for the production of nitroguanidine (picrite) from urea in order to introduce possible improvements and define more exact conditions for a continuous process.

(ii) A preliminary economic assessment of the process be made for its evaluation relative to any other alternative route to nitroguanidine.

and (iii) A comprehensive study of the chemical changes involved at the various stages in the process be carried out in order to define the character of by-products.

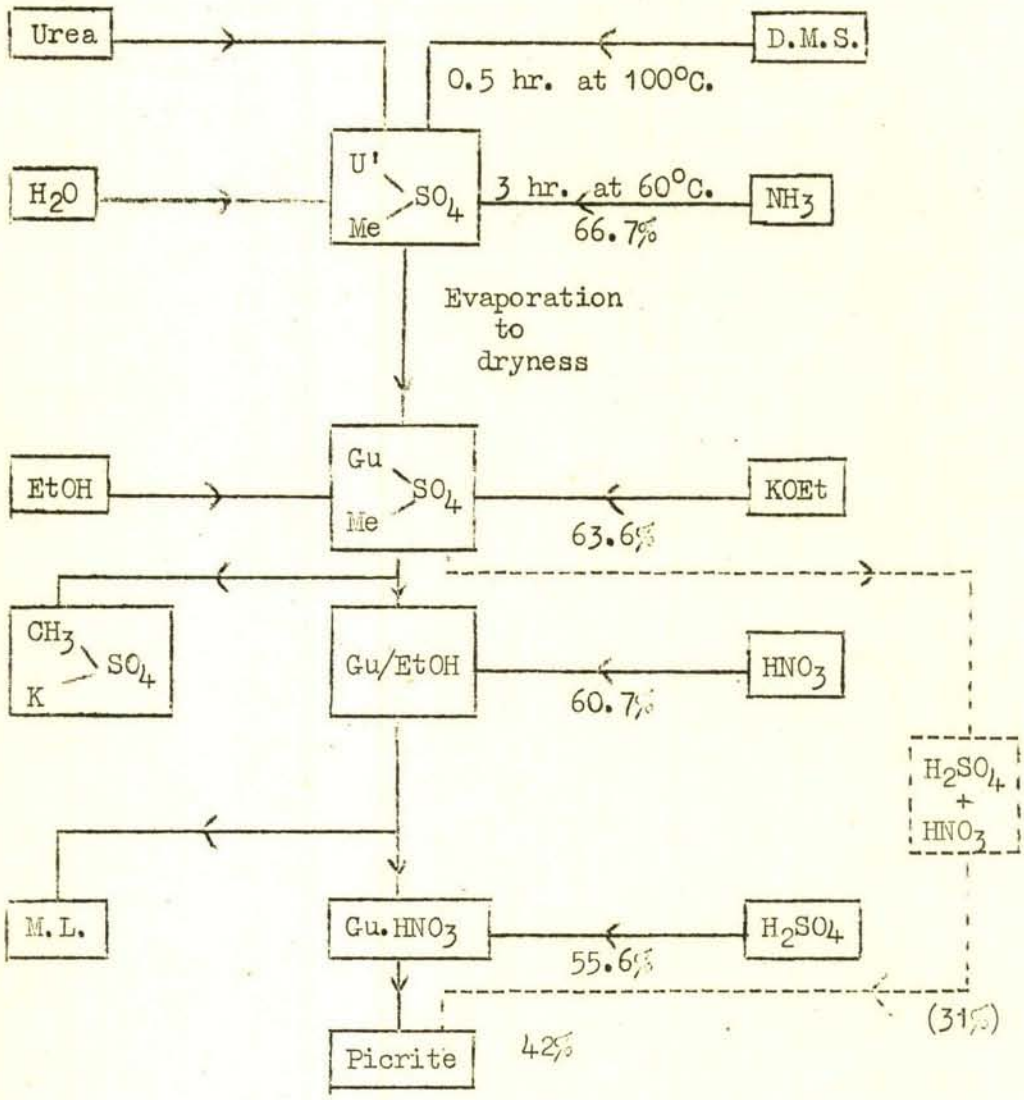
1. Introduction

Previous work (1) showed that guanidine could be synthesised from urea by methylation, using dimethyl sulphate under anhydrous conditions and in the absence of bases, followed by amination of the product, O-methylisourea.

In order to assess this route to guanidine, viz. etherification of urea followed by amination, the relative efficacy of etherifying agents, other than dimethyl sulphate, was investigated (2) in order to choose the most suitable agent for a more comprehensive study of a process for the production of guanidine and nitroguanidine from urea. It was shown that the best agents, of those examined, for the etherification, i.e. O-alkylation, of urea are the dialkyl sulphates working under anhydrous conditions and in the absence of bases and solvents. The optimum yields of guanidine using dimethyl-, diethyl-, di-n-propyl- and di-n-butyl sulphates are 60, 72, 72 and 75 per cent respectively. Of these, only dimethyl sulphate and diethyl sulphate were considered worthy of further consideration since they are available commercially. Owing to the lower yield when using dimethyl sulphate and its poisonous nature a further study of the use of diethyl sulphate was warranted for the development of a process for the production of guanidine and/or its salts, based on urea, and its conversion to nitroguanidine.

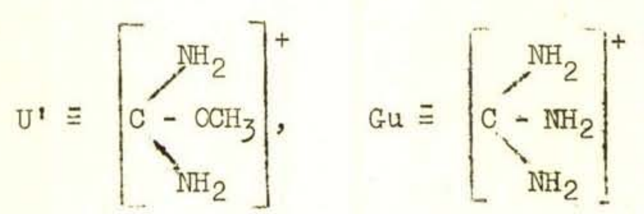
In the initial work (1) a close study was made of the reaction between dimethyl sulphate and urea and the optimum conditions for methylation and subsequent amination ascertained. The guanidine was isolated as a salt, guanidine nitrate, which was then nitrated to give nitroguanidine. The original scheme for making nitroguanidine (picrite) from urea was as follows:

Molar Ratio Urea : Dimethyl-sulphate (D.M.S.) = 1:1



Note:

(i)



O-methylisourea Guanidine

(ii) The per cent values in table show the overall yield at each stage based on urea. Further investigation would not doubt show an improved yield of nitroguanidine by this route.

This scheme for the production of nitroguanidine from urea is attractive, but it has certain drawbacks, for example, (a) the use of anhydrous alcohol and an alcoholic solution of potassium ethoxide, (b) recycle of methyl potassium sulphate, CH_3KSO_4. The latter would entail making potassium sulphate in quantity in the recovery of the methyl group as dimethyl sulphate. It is an essential however in any efficient process to establish closed cycles, that is, to rework all by-products into the working cycle.

The possibility of overcoming the drawbacks enumerated above was envisaged and a promising process for the production of nitroguanidine from urea has been developed. The essential steps in this new process are represented schematically as follows:

$$\begin{array}{l}\quad NH_2 \\ \;/ \\ CO \\ \;\backslash \\ \quad NH_2\end{array} \rightleftharpoons \begin{array}{l}\quad NH_2 \\ \;/ \\ C - OH \\ \;\backslash\backslash \\ \quad NH\end{array}$$

Urea — Isourea

$$\begin{array}{l}\quad NH_2 \\ \;/ \\ C - OH \\ \;\backslash\backslash \\ \quad NH\end{array} + Et_2SO_4 \xrightarrow{\text{Ethylation}} \begin{array}{l}\quad NH_2 \\ \;/ \\ C - OEt \\ \;\backslash\backslash \\ \quad NH\end{array} + EtHSO_4 \longrightarrow \left[\begin{array}{l}\quad NH_2 \\ \;/ \\ C - OEt \\ \;\backslash \\ \quad NH_2\end{array}\right]^{+} EtSO_4^{(-)} \quad \text{- (i)}$$

O-Ethylisourea

$$\left[\begin{array}{l}\quad NH_2 \\ \;/ \\ C - OEt \\ \;\backslash \\ \quad NH_2\end{array}\right]^{+} EtSO_4^{(-)} + NH_3 \xrightarrow{\text{Amination}} \left[\begin{array}{l}\quad NH_2 \\ \;/ \\ C - NH_2 \\ \;\backslash \\ \quad NH_2\end{array}\right]^{(+)} EtSO_4^{(-)} + EtOH \qquad \text{(ii)}$$

Guanidinium Ethyl sulphate

$$\left[\begin{array}{l}\quad NH_2 \\ \;/ \\ C - NH_2 \\ \;\backslash \\ \quad NH_2\end{array}\right]^{+} EtSO_4^{(-)} + H_2O \xrightarrow{\text{Hydrolysis}} \left[\begin{array}{l}\quad NH_2 \\ \;/ \\ C - NH_2 \\ \;\backslash \\ \quad NH_2\end{array}\right]^{(+)} HSO_4^{(-)} + EtOH \qquad \text{(iii)}$$

Guanidinium Hydrogen sulphate

$$\left[\begin{array}{l}\quad NH_2 \\ \;/ \\ C - NH_2 \\ \;\backslash \\ \quad NH_2\end{array}\right]^{+} HSO_4^{(-)} + HNO_3 \xrightarrow{\text{Nitration}} \begin{array}{l}\quad NHNO_2 \\ \;/ \\ C - NH_2 \\ \;\backslash\backslash \\ \quad NH\end{array} + H_2O + H_2SO_4 \qquad \text{(iv)}$$

Nitroguanidine
(Picrite)

Some important features governing the use of diethyl sulphate in this process are: (a) the recovery of the ethyl groups as alcohol which can be recycled if necessary, and (b) the conversion of the sulphate radical into free sulphuric acid which can be usefully employed in the nitration stage (iv).

In view of the interest shown in the present development the progress achieved, so far, is now reported.

2. Alkylation of urea with diethyl sulphate and the conversion of O-ethylisourea to guanidine

A further study of the parameters governing the yield of guanidine, based on urea, has been made.

Previous work (2) had shown that, using the molar ratio urea : diethyl sulphate, 1 : 1, ethylating at 100°C. and aminating the product in aqueous solution a yield of ca. 70 per cent guanidine could be obtained. When the reaction was carried out at 155°C. using the molar ratio, urea : diethyl sulphate, 2 : 1, then a very low yield of guanidine was obtained; the use of these reaction conditions is analogous to those employed (3) for the production of S-methyl thiourea when both methyl groups of the alkylating agent, dimethyl sulphate, are utilised.

It has now been shown that when the molar ratio of urea : diethyl sulphate is varied, and ethylating at 100°C. for 1 hour, followed by amination of the product in aqueous solution at 60°C. for 3 hours, the yields of guanidine, based on urea (in brackets corresponding yields on diethyl sulphate are given), for the molar ratios, diethyl sulphate : urea, 1 : 0.8, 1 : 0.9, 1 : 1.0, 1 : 1.1, 1 : 1.2, 1 : 1.5 and 1 : 2.0 are 74.2 (59.3), 72.5 (65.2), 71.8 (71.8), 71.5 (78.6), 66.7 (80.1), 53.7 (80.5) and 40.2 (80.4) per cent respectively. The yields, relative to urea or alkylating agent would have to be considered for any projected process. These yield data indicate the molar ratio, diethyl sulphate : urea, 1.0 : 1.2 to be the most economical, on the assumption that diethyl sulphate is the more costly reactant. This ratio was therefore chosen for closer investigation in connection with the initial scheme for the production of nitroguanidine, indicated in Section 1, above.

Using the molar ratio diethyl sulphate : urea, 1.0 : 1.2, the effect of temperature of alkylation and time of reaction on the yield of guanidine was investigated. Amination of the product of ethylation was effected in aqueous solution at 60°C. for 3 hours. At 80°C. the yields of guanidine, based on urea (in brackets corresponding yields based on diethyl sulphate are given), after 90, 120, 150 and 160 mins., are 60.1 (72.1), 62.5 (75.0), 64.2 (77.0), and 64.9 (77.9) per cent respectively. At 90°C. the yields of guanidine, based on urea (in brackets corresponding yields based on diethyl sulphate), after 30, 60, 90 and 120 mins., are 53.6 (64.2), 63.7 (76.5), 66.2 (99.4) and 66.9 (80.30) per cent respectively. At 100°C. the yields of guanidine, based on urea (in brackets corresponding yields based on diethyl sulphate), after 30, 60 and 90 mins., are 64.3 (77.1), 67.0 (80.4) and 66.3 (79.6) per cent respectively. At 110°C. the yields of guanidine, based on urea (in brackets corresponding yields based on diethyl sulphate), after 15, 30 and 60 mins., are 66.3 (79.6), 67.0 (80.4) and 66.2 (79.4) per cent respectively. At 120°C. the yields of guanidine, based on urea (in brackets corresponding yields based on diethyl sulphate), after 5, 10 and 15 mins., are 64.6 (77.6), 66.1 (79.3) and 66.1 (79.3) per cent respectively. These results indicate that the ethylation of urea is optimum after 2 hours at 90°C., 1 hour at 100°C., or 0.5 hour at 110°C. In practice it is preferred to operate at 100°C. or 110°C.

At a later stage of the work the process for the production of nitroguanidine from urea, came under review. From considerations of yield data based on urea it was desirable to carry out a similar series of experiments using the molar ratio, urea : diethyl sulphate, 1.0 : 1.0. The effect of temperature of alkylation and time of reaction was investigated; amination of the product of ethylation was effected in aqueous solution at 60°C. for 3 hours. At 100°C. the yields of guanidine, based on urea, after 15, 30, 60 and 90 mins. are 60.4, 65.6, 69.7 and 72.3 per cent respectively. At 110°C. the yields of guanidine, based on urea, after 15, 30, 45 and 60 mins. are 67.9, 71.1, 70.6 and 71.5 per cent respectively. At 120°C. the yields of guanidine, based on urea, after 5, 10, 15 and 20 mins. are 65.4, 69.3, 69.7 and 70.4 per cent respectively. These results indicate that the ethylation of urea is optimum after 1 hour at 100°C., 0.5 hour at 110°C., or 15-20 mins. at 120°C. Any of these reaction temperatures could be utilised in practice, although a finer definition of the reaction temperature in terms of very small yield differences and the nature of the by-products of reaction may be necessary at a later stage of development.

The amination of reaction mixtures containing O-ethyl-isourea was studied using gaseous ammonia; this work is described below. It was found that no ammonia was absorbed corresponding to the titratable acidity of the reaction mixture. It was considered however that this acidity might be due to the present of an urea salt in the reaction mixture and, as it had already been shown (2) that salts of urea do not react with alkyl sulphates, this might account for the low yields obtained in the alkylation stage. Accordingly some alkylation experiments were carried out with addition of pyridine to take up free acidity in place of urea. Using the molar ratio, urea : diethyl sulphate, 1.0 : 1.0, and ethylating at 100°C. in presence of 0.05 mole pyridine per mole diethyl sulphate, and at 110°C., in presence of 0.10 mole pyridine per mole diethyl sulphate, for 0.5 hour, followed by amination of the product in aqueous solution at 60°C. for 3 hours, the yields of guanidine, based on urea, are 67.1 (65.7) and 69.0 (71.1) per cent respectively; in brackets are given the yields of guanidine in parallel experiments, without addition of pyridine. The results indicate that no apparent advantage accrues on addition of a base, e.g. pyridine, at the alkylation stage. Similar experiments will be conducted in the presence of anhydrous ammonia when the relative rates of ethylation plus amination to give guanidine and N-ethylation of ammonia will be compared. The complete significance of the titratable acidity, formed in general on alkylation of urea, has not as yet been investigated.

3. Heat evolution in the reaction between urea and diethyl sulphate

The alkylation stage consists in adding the whole of the urea, i.e. in one lot, to the diethyl sulphate preheated to the reaction temperature; some preliminary experiments have shown (2) that the yield of guanidine is independent of the rate of addition of urea. This usually results in lowering the temperature of the reaction mixture which is then raised to the required reaction temperature. A two liquid phase reaction mixture is obtained initially, and as the reaction proceeds a mono liquid phase system is obtained. The reaction between urea and diethyl sulphate is slightly exothermic and therefore must be controlled.

Experiments were carried out to observe the extent of heat evolution during the ethylation of urea with diethyl sulphate, using the molar ratio 1 : 1, and the maximum temperature likely to be obtained if the temperature of the reaction mixture were not controlled. In one experiment a stirred mixture of urea and diethyl sulphate was inserted in a bath at 100°C. when the reaction temperature rose to 120°C. The temperature was then controlled at this temperature for 15 mins. and then analysed for total acidity and O-ethylisourea, indirectly by conversion to guanidine, in the usual way. Mean values showed a total acidity of 8.1 per cent, as $EtHSO_4$, on diethyl sulphate and a yield of 70.2 per cent guanidine. In another experiment no attempt was made to control the reaction temperature after immersion of reactants in the bath at 100°C. The maximum temperature recorded was 124°C. when it again fell to 100°C. after 7 mins. The reaction mixture was analysed at this stage. Mean values showed a total acidity of 11.0 per cent as $EtHSO_4$, on diethyl sulphate, and a yield of 66.0 per cent guanidine; the reaction was apparently not complete under the time temperature conditions investigated.

The observations indicate that no danger existed in the reaction going completely out of control. The maximum temperature obtained if the reaction were not controlled would be determined by the degree of insulation. Earlier work has shown (1) that in general the yield of O-alkylisourea tends to diminish at temperatures over 120°C. The total heat of reaction is apparently not of a high order and will be measured more accurately in subsequent work.

4. Alkylation of urea using di-isopropyl sulphate

An assessment has been made (2) of the relative efficiency of the lower normal dialkyl sulphates in the alkylation of urea. It was suggested, in view of the increasing potential of propylene supplies and its ease of conversion to di-isopropyl sulphate, that a study of the alkylation of urea be made using di-isopropyl sulphate.

Di-isopropyl sulphate as supplied commercially is a dark coloured oil of purity ca. 93 per cent. The material can be dried to neutrality by standing over anhydrous potassium carbonate. The neutral material on distillation in vacuo gave a small quantity of colourless distillate, almost pure di-isopropyl sulphate, but a vigorous decomposition set in with evolution of gas, propylene, during the distillation which was then discontinued. The distillation residue was dark and strongly acid. The distillate, B.P. 76°C./2 mm., soon developed a purple colour on standing and is unstable at ordinary temperatures; it develops an acidity which progressively increases on storage.

Alkylation of urea was studied using the redistilled ester and also the deacidified crude material.

Using redistilled ester and the molar ratio, urea : di-iso-propyl sulphate, 1 : 1, alkylation was carried out at 100°C. for 1 hour followed by amination of the product in aqueous solution at 60°C. for 3 hours. During the alkylation considerable gas evolution occurred and the originally colourless reaction mixture developed a dark reddish purple colouration. Analysis of the reaction mixture showed a total acidity of 30 per cent $PrHSO_4$, on Pr_2SO_4, and a yield of 44.6 per cent guanidine, on urea.

Using the commercial grade of ester and the molar ratio, urea : di-iso-propyl sulphate, alkylation was carried out at 80°C. for a period of 2 hours. This reaction temperature was chosen in view of the degradation observed at 100°C. when using the redistilled ester. There was little development of colour and only a slow evolution of gas. The product of alkylation was aminated in the usual way and analysed. It showed a total acidity of 34 per cent $PrHSO_4$, on Pr_2SO_4, and a yield of 48.5 per cent guanidine, on urea.

In view of the intrinsic instability of di-isopropyl sulphate and the low yields of guanidine obtained this investigation was discontinued.

5. Attempts to alkylate urea directly by use of ethylene and isobutylene

It was suggested that the alkylation of urea might be effected directly by use of ethylene, and isobutylene, working under slightly acid conditions. This suggestion has been investigated, although not exhaustively.

Ethylene. (i) Using the molar ratio, urea : diethyl sulphate, 1 : 1, alkylation was effected at 100°C. for 1 hour. During this whole period a rapid stream of ethylene was passed through the reaction mixture. No increase in weight of reaction mixture and therefore no apparent absorption of ethylene occurred under these conditions. A portion of the reaction product was examined for acidity, and aminated in the usual way. Analysis showed a yield of 68.8 per cent guanidine, on urea or diethyl sulphate.

(ii) To the bulk of the alkylation product, from (i), was added a further quantity of urea (0.5 mol). The mixture was heated to 100°C. when a clear liquid was obtained. This was stirred at 100°C. whilst sulphuric acid equivalent (0.5 mol.) to the urea was slowly added dropwise and a rapid current of ethylene passed through the reaction mixture. No increase in weight of the reaction mixture and therefore no apparent absorption occurred

under these conditions. Portions of the reaction product, a brown viscous liquid which crystallised on standing to give a solid (F.P. 42°C.), was examined for total acidity and aminated in the usual way. Analysis showed a yield of 80.7 per cent guanidine, on diethyl sulphate used.

The use of the molar ratio, urea : diethyl sulphate, 1 : 1, in the first part of the experiment gave a 68.8 per cent yield of guanidine, based on diethyl sulphate. In the second part of the experiment the molar ratio of urea : diethyl sulphate was 1.5 : 1.0 when the yield of guanidine was 80.7 per cent based on diethyl sulphate. Earlier work (this report, section 2) showed that yields of guanidine using the molar ratios, urea : diethyl sulphate, 1 : 1 and 1.5 : 1 are 71.8 and 80.4 per cent respectively. It therefore seems probable that the increased yield of guanidine observed in the second part of the experiment is solely due to the addition of further urea, i.e. change of concentration, to the reaction mixture and not to any consumption of ethylene.

Isobutylene. Similar experiments to those described, using ethylene, were carried out using isobutylene.

(i) Using the molar ratio, urea : diethyl sulphate, 1 : 1, ethylation was effected at 100°C. for 1 hour whilst a rapid stream of isobutylene was passed through the reaction mixture. No increase in weight of reaction mixture occurred and therefore no apparent absorption of isobutylene occurred under these conditions. Portions of the reaction product were examined for acidity and aminated in the usual way. Analysis showed a yield of 68.2 per cent on diethyl sulphate.

(ii) To the bulk of the reaction product from (i) was added a further quantity of urea (0.25 mol.). The mixture was heated to 100°C. when a clear liquid was obtained. This was stirred at 100°C. whilst sulphuric acid equivalent (0.25 mol.) to the urea was slowly added dropwise and a rapid current of isobutylene passed through the reaction mixture. As the gas was passed the reaction mixture became progressively darker in colour, and on cooling a viscous liquid was obtained which did not solidify on prolonged standing. An increase in weight of the reaction mixture was observed showing that isobutylene had been absorbed. Portions of the reaction product were examined for acidity and aminated in the usual way. Analysis showed a yield of 75.3 per cent guanidine, on diethyl sulphate used.

As in the case of ethylene the increase in yield of guanidine is not more than would be expected by increasing the urea ratio from 1.0 to 1.25 moles per mol. diethyl sulphate (this report, section 2). The absorption of isobutylene is not accompanied by any decrease in acidity, and is due to its polymerisation in contact with sulphuric acid.

In a quantitative test experiment it was shown that isobutylene is absorbed by concentrated H_2SO_4 at 20-25°C. with considerable evolution of heat. The reaction product becomes progressively darker in colour, and on standing separates into two layers. The dark lower acid layer showed only a slight change in acid content whilst the upper layer was water white and consisted mainly of polyisobutene; the latter was not investigated further.

6. The amination of O-ethyl-isourea

$$\left[\begin{array}{l} \quad NH_2 \\ \;/ \\ C - OEt \\ \;\backslash \\ \quad NH_2 \end{array} \right] EtSO_4 + NH_3 \longrightarrow \left[\begin{array}{l} \quad NH_2 \\ \;/ \\ C - NH_2 \\ \;\backslash \\ \quad NH_2 \end{array} \right] EtSO_4 + EtOH$$

In our work it is understood that amination is conducted using the reaction mixture derived by alkylation of urea using diethyl sulphate. The reaction mixture contains a high percentage, ca. 70-73 per cent, of O-ethylisourea as a salt of ethyl hydrogen sulphate and impurities, the exact nature of which are as yet to be investigated.

In previous work (2) a quantitative study was made of the conversion of O-ethylisourea to guanidine in aqueous solution and it was shown to be almost quantitative using 20 per cent excess ammonia and heating at 60°C. for 3 hours.

It was considered desirable to investigate the conversion in an anhydrous solvent, e.g. ethyl alcohol, in accord with the initial scheme for isolating the guanidine from the reaction product by use of potassium ethoxide in ethyl alcohol solution. Furthermore, since ethyl alcohol is liberated on amination of O-ethylisourea it was necessary to investigate the direct amination of the alkylation product by use of anhydrous gaseous ammonia.

A quantitative study was made of the conversion of O-ethylisourea to guanidine in ethyl alcohol solution at 60°C. varying the concentration of alcohol and ammonia (gas) and also the time of reaction. In general it was observed that the rate of amination at 60°C. was rapid, and using 0.8 to 1.0 moles NH_3 per mole urea used for ethylation the extent of amination after 0.5 hr. and 3 hrs. was ca. 65 and 80 per cent respectively of the maximum possible; the maximum possible was that determined by aqueous amination at 60°C. for 3 hrs. The rate and extent of amination appeared to be only slightly dependent on the alcohol concentration. This study was not exhaustive and was abandoned in view of the success attained by direct amination of the original product of the ethylation stage.

The direct amination of the product obtained at the ethylation stage has been effected using gaseous ammonia. Several batches, using the molar ratios, urea : diethyl sulphate, 1 : 1 and 1.2 : 1, have been aminated.

The general procedure is to cool the product of ethylation, when alkylation is completed either at 100°C. for 1 hour, or 110°C. for 30 min., to 60°C. and then pass dry gaseous ammonia at such a rate that it is completely absorbed; the rate of absorption is rapid. The absorption of ammonia is accompanied by evolution of heat and the reaction mixture is maintained, by slight cooling, at 60°C. As amination proceeds the reaction mixture becomes progressively less viscous owing to the liberation of alcohol and when amination is complete it is quite mobile. Amination appears to be complete when no further liberation of heat occurs on continued passage of ammonia. In general an excess of ammonia is used which can subsequently be recycled. After amination the product has usually been allowed to stand overnight when crystallisation sets in; using the molar ratio, urea : diethyl sulphate, 1 : 1, the solid is completely soluble at about 45°C. The product is freed from alcohol by heating under slowly diminishing pressure but gradually raising the temperature of the bath to 100°C. Finally it is heated at 100°C. at 1-2 mm., in order to recover all the alcohol for assessment; the freezing point of the material is ca. 94°C. The alcohol distillate usually contains a minute amount of a white solid which has been shown to be ammonium carbonate.

The amination of O-ethyl isourea proceeds rapidly and quantitatively under the conditions investigated. It has however been observed that the amount of alcohol recovered at this stage is in general equivalent to the guanidine formed. Moreover, it has also been observed that the yield of guanidine, based on urea, obtained by this procedure is about 2-3 per cent greater than that attained by aqueous amination of the product of ethylation. This increment in yield would only appear to be accounted for by a displacement of urea by ammonia

in a possible equilibrium involving urea and diethyl sulphate at the ethylation stage; this point will be studied later in greater detail.

A more detailed examination of this amination stage is to be made later in order to define the optimum conditions for technical operation.

7. Action of heat on guanidinium ethyl sulphate

The salt, O-ethyl isourea ethyl sulphate, contained in the product of alkylation, is converted quantitatively on amination to guanidinium ethyl sulphate. The isolation of guanidine, in a form amenable to direct nitration, was an outstanding problem. In early work (1) it had been shown that treatment of guanidinium alkyl sulphate in alcoholic solution by use of potassium alkoxide gave free guanidine and the almost insoluble potassium alkyl sulphate. It had been shown that excellent yields of diethyl sulphate could be obtained either by heating sodium ethyl sulphate in vacuum (4), or, by heating a mixture of ethyl hydrogen sulphate and sodium sulphate in vacuum (5). By analogy, since guanidinium hydroxide is as strong a base as either sodium or potassium hydroxide, the conversion of guanidinium ethyl sulphate to guanidinium sulphate and diethyl sulphate was considered feasible. Attempts were made to effect this conversion but without success.

The material obtained by aminating, using gaseous ammonia, the product of alkylation was freed from alcohol, as indicated heretofore, and used for investigation; the material contained a high percentage of guanidinium ethyl sulphate and impurities, the exact nature of which are as yet to be investigated.

The material containing guanidinium ethyl sulphate on gradual heating at atmospheric pressure for prolonged periods at 140°C. (10 mins.), 165°C. (30 mins.), 185°C. (5 mins.) and 210°C. (60 mins.) showed but apparent slight degradation. A small amount of colourless gas was evolved which was readily soluble in alkali and therefore apparently was not ethylene. On analysis however it was shown that there was a loss of guanidine corresponding to 33.6 per cent.

The material on gradual heating under diminished pressure, 1 to 3 mm., at 120°C. to 225°C. showed but very little apparent degradation. At first there appeared to be slight evolution of gas and the material seemed to boil at 225°C./1-3 mm. but no distillate was collected. The temperature of the mass was finally raised and maintained at 260°C.-280°C./1-3 mm. Under these conditions there appeared to be vigorous boiling, but no distillate was collected; also, the material became discoloured and heating was discontinued. The residue was a dark brown viscous material, readily soluble in water. A loss of weight of material corresponding to 37 per cent was observed, but only a small quantity of ammoniacal liquor was found in the cold traps of the vacuum system.

In view of the marked degradation observed on heating this part of the investigation was discontinued.

8. The hydrolysis of guanidinium ethyl sulphate

$$\left[\begin{array}{l} \quad NH_2 \\ \ / \\ C - NH_2 \\ \ \backslash \\ \quad NH_2 \end{array}\right] EtSO_4 + H_2O \xrightarrow{H_2SO_4} \left[\begin{array}{l} \quad NH_2 \\ \ / \\ C - NH_2 \\ \ \backslash \\ \quad NH_2 \end{array}\right] HSO_4 + EtOH$$

Potassium and sodium ethyl sulphate, on hydrolysis in aqueous acid solution give ethyl alcohol and presumably potassium and sodium sulphates. As far as

can be ascertained this hydrolysis has not been studied quantitatively with the view to recovery of alcohol. This observation seemed well adapted to the case of guanidinium ethyl sulphate, and merited thorough investigation, since the product of hydrolysis, viz. guanidinium hydrogen sulphate, would be amenable to nitration, and, furthermore the recovery of the ethyl group in the form of ethyl alcohol was most attractive.

The material obtained by aminating, using gaseous ammonia, the product of alkylation was freed from alcohol, as indicated heretofore, and used for investigation.

In preliminary work it was observed that when the material, product from the amination stage, was refluxed with a small quantity of N/1 sulphuric acid the reaction mixture became alkaline due to liberation of ammonia. As the amount of sulphuric acid was increaseda point was reached when the reaction mixture ceased to show alkalinity but to show an acidity greatly in excess of that added in the form of N/1 sulphuric acid. Furthermore the boiling point of the reaction mixture gradually fell during the reflux period showing unmistakably that hydrolysis had been effected. On the basis of these observations a quantitative study was made to determine the optimum acid concentration for complete hydrolysis of guanidinium ethyl sulphate, maximum recovery of ethyl alcohol and minimum loss of guanidine.

The general procedure was to add varying quantities of concentrated sulphuric acid to constant amounts of material, product from amination stage, and water; the weight of water used was ca. 30 per cent on the weight of material. The mixture was refluxed until the hydrolysis appeared complete; this was indicated by the attainment of a steady minimum for the boiling point of the liquid; usually the original boiling point was ca. 117°C. and the final boiling point ca. 98°C. The reaction mixture was then carefully fractionated at normal pressure, distillate being accepted until the boiling point of the liquid reached 120-125°C. The distillate was weighed and the alcohol content estimated by determination of its density. All remaining alcohol and water was then distilled, under diminished pressure and finally at 20-30 mm., bath temperature 100°C., and collected; the weight and alcohol content of distillate was determined. The distillation residue was analysed for total acidity and guanidine content.

Using 100 parts amination product and 28 parts H_2O, hydrolysis was effected using 3.2 (90), 4.0 (90), 6.2 (90), 8.0 (30), 10.0 (15), 12.0 (10) and 3.6 (5) parts (100 per cent) H_2SO_4; in brackets are given the corresponding time for apparent complete hydrolysis. When using 3.2 parts H_2SO_4 hydrolysis proceeded about 30 per cent when the reaction mixture became neutral. In all other cases hydrolysis was complete, the time for hydrolysis progressively diminishing with increase in concentration of sulphuric acid.

The total amount of alcohol recovered is of the order of 47-48 per cent on the original diethyl sulphate used, of which 70 per cent was recovered as first distillate at 82-85 per cent concentration and 30 per cent as second distillate at 30-33 per cent concentration.

The free sulphuric acid liberated on hydrolysis of guanidinium ethyl sulphuric should be equivalent to the ethyl group recovered as alcohol. In general however the total acid freed is less than theory and corresponds to a fixation i.e. as neutral salt equivalent to about 4 per cent of the acid added to promote hydrolysis plus that required by theory. It has, however, been observed in general that about 77 per cent of the original sulphate radical in diethyl sulphate is distributed, after hydrolysis, as free sulphuric acid and fixed as guanidine sulphate; this sulphuric acid is usefully employed in the nitration stage (see below).

The calculated amount of water remaining in the distillation residue, guanidinium hydrogen sulphate plus impurities, is relatively small. Nearly all the water has been volatilised together with the alcohol. The water content of a typical distillation residue was determined by Karl Fischer reagent and showed to be of the order of 1 per cent. It would appear therefore that the distillation residue consists primarily of acid sulphates which are readily freed from water at relatively low temperatures, viz. 100°C. at 20-30 mm. If the residue contained free sulphuric acid in reasonable quantity then dehydration would be more difficult.

A more critical examination of the hydrolysis stage is to be made in order to establish optimum conditions for technical operation.

9. Preparation of guanidinium hydrogen sulphate

On the basis of studies of the alkylation, amination and hydrolysis stages, a number of large batches of the material containing guanidinium hydrogen sulphate were prepared. These preparations provided further observation on the various stages involved, and material for study of the nitration stage (see below).

Preparations were made using the molar ratios, urea : diethyl sulphate, 1.0 : 1.0 and 1.2 : 1.0. In view however of the success attending the hydrolysis stage (section 8) in which alcohol and sulphuric acid, i.e. in original diethyl sulphate, are efficiently recovered the use of the molar ratio, 1.0 : 1.0, was preferred. Furthermore, by use of this ratio the amount of nitrogenous impurities at the end of the distillation stage would be somewhat lower, and would thus afford some advantage at the subsequent nitration stage.

In general ethylation, amination and hydrolysis were effected in one and the same vessel in order to minimise losses. The working details were as described heretofore. Using the molar ratio, urea : diethyl sulphate, 1.0 : 1.0 the ethylation was carried out at either 100°C. for 1 hour or 110°C. for 30 mins. The ethylated product showed a freezing point of ca. 64°C. Amination of the product was effected at 60°C. and the final reaction mixture was usually allowed to stand overnight. At this stage the recovery of alcohol was of the order of 40 per cent on diethyl sulphate. The product of amination usually crystallised at 35-40°C., and after recovery of alcohol the freezing point of the residue was ca. 94°C. Hydrolysis of the amination product was carried out using 100 parts product, 28 parts water and 10 parts H_2SO_4. During hydrolysis, time 30 mins., the boiling point fell from ca. 118°C. to 104°C. The recovery of alcohol at this stage was usually of the order of 42 per cent on diethyl sulphate. The amount of H_2SO_4 fixed as neutral salt at the hydrolysis stage was of the order of 2-4 per cent. The product of hydrolysis is liquid at room temperature, and after recovery of alcohol and water the freezing point of the residue was ca. 63°C. In order to avoid crystallisation of this residue it was diluted with a known amount of concentrated sulphuric acid whilst still warm when an appreciable amount of heat is liberated. This marked liberation of heat is not due entirely to solution effects and is attributed to a definite reaction the precise nature of which has not been ascertained. There is however no loss of guanidine on addition of sulphuric acid. The solution of guanidinium hydrogen sulphate in concentrated sulphuric acid was used in subsequent nitration studies (see below).

The change in guanidine content during the various stages of the reaction has been followed analytically and the following data are typical. The percentage yields of guanidine, based on urea, were:

(a) at ethylation stage, aqueous amination showed 68.6 per cent;

(b) amination stage, (i) before expelling alcohol, 72.2 per cent, (ii) after expelling alcohol, 72.2 per cent;

(c) hydrolysis stage, (i) before expelling alcohol, 72.8 per cent (ii) after expelling alcohol, 72.7 per cent.

Consistent yields of guanidine of the order of 72-73 per cent, based on urea, were obtained in all preparations of guanidinium hydrogen sulphate. The difference in yield, ca. 2-3 per cent, observed on aqueous and gaseous amination of the product of ethylation has previously been commented upon (this report section 6).

Composition of hydrolysis product containing guanidinium hydrogen sulphate, Gu HSO_4

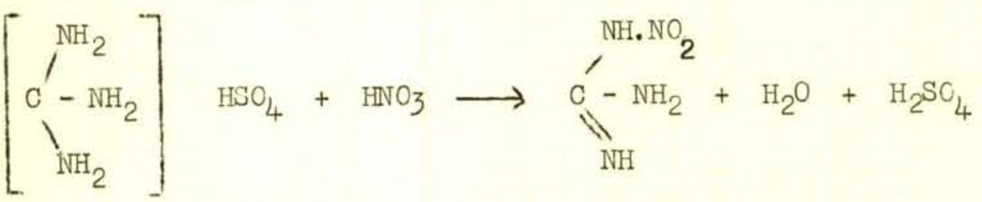
A typical analysis of the product of hydrolysis, F.P. 63°C., prepared using the original molar ratio, urea : diethyl sulphate, 1 : 1, is shown below.

Composition	%
Guanidine	22.70
Bases as $(NH_4)_2SO_4$	7.45
Free H_2SO_4	31.13
H_2SO_4 fixed as Gu_2SO_4	18.86
Potential N as $(NH_4)_2SO_4$	99.68

The stability to heat of a solution of guanidinium hydrogen sulphate, Gu HSO_4, in concentrated sulphuric acid

When a solution of guanidinium sulphate in concentrated sulphuric acid containing the molar ratio, guanidine: H_2SO_4, 1.0 : 2.0, was heated successively at 60°C. (1 hour), 80°C. (1 hour), and 100°C. (1 hour) no change in guanidine content was observed.

10. Nitration of guanidinium hydrogen sulphate



Note: By guanidinium hydrogen sulphate, Gu HSO_4, is meant the product of hydrolysis which has been almost totally freed of alcohol and water by distillation. The product contains a high percentage of guanidine, ca. 72-73 per cent, based on urea, as guanidinium salt and impurities, the exact nature of which are as yet to be investigated.

The nitration of $GUHSO_4$, batches of which were prepared as described in section 9, was studied in order to examine its behaviour and define the conditions for maximum conversion to nitroguanidine. The order of study of the various parameters was arbitrary. The choice of successive parameters was determined usually by earlier results. The work was conducted in this manner in order to achieve a more rapid assessment of the nitration stage.

General method. A quantity of the molten or supercooled guanidinium hydrogen sulphate material was stirred with the requisite quantity of concentrated, 98 per cent, sulphuric acid, when a marked evolution of heat

occurred. If excessive cooling was applied at this stage the material tended to solidify and did not then dissolve readily in the sulphuric acid. When the sulphuric acid, using our weight ratios, was added without temperature control, to the supercooled material at ordinary temperature the final temperature would be ca. 55°C.

The sulphuric acid solution was cooled and the requisite quantity of 98 per cent nitric acid added slowly with good stirring the nitration temperature being maintained by external cooling. When addition of nitric acid was complete the reaction mixture was stirred for a further period of time at the nitration temperature. It was then drowned on to a sufficient quantity of ice and water to dilute the sulphuric acid present to 20 per cent concentration. The precipitated nitroguanidine was allowed to stand a few minutes with occasional stirring in order to ensure the conversion of any salt, nitroguanidine sulphate, to nitroguanidine. This was filtered, well washed with water (in initial experiments) or a saturated (at room temperature) solution of nitroguanidine in final experiments, retransferred to the precipitating vessel and triturated with a further quantity of wash medium. It was again filtered and washed, then dried, usually overnight, to constant weight at 100°C.

The most important parameters studied were: molar ratio, Gu : H_2SO_4 : HNO_3, temperature and time of nitration. The experimental conditions together with yield data are summarised below:

Series	Molar Ratio /mole Gu $H_2SO_4:HNO_3$	Temp, of Nitration °C.	Time of addn. of HNO_3 mins.	Time of stirring after addn. of HNO_3 mins.	Nitn. Stage yield of Nitro-guanidine %	Notes
I 1	2.06:1.06	25-30	10	180	61.6	(1)(3)(4)
2	2.04:1.30	"	"	"	64.1	(1)(3)(4)
3	2.58:1.04	"	"	"	58.0	(1)(3)(4)
4	2.53:1.28	"	"	"	69.5	(1)(3)(4)
5	3.13:1.14	"	"	"	63.2	(1)(3)(4)
II 1	2.04:1.30	20	10	50	63.5	(1)(5)
2	2.59:1.32	20	10	60	74.6	(1)(6)
III 1	2.07:1.0	0	10	60	17.2	(1)(7)
2	2.07:1.0	20	8	"	48.4	(1)(7)
3	2.07:1.25	0	13	"	32.9	(1)(7)
4	2.07:1.25	20	11	"	59.7	(1)(7)
5	2.59:1.0	0	8	"	62.3	(1)(7)
6	2.59:1.0	20	10	"	67.0	(1)(7)
7	2.59:1.25	0	10	"	72.8	(1)(7)
8	2.59:1.25	20	11	"	77.0	(1)(7)
9	3.11:1.0	0	8	"	71.4	(1)(7)
10	3.11:1.0	20	9	"	65.3	(1)(7)
11	3.11:1.25	0	11	"	84.0	(1)(7)
12	3.11:1.25	20	15	"	78.1	(1)(7)
IV 1	4.15:1.39	0	12	60	82.7	(1)(8)
2	4.15:1.0	20	9	"	64.4	(1)(8)
3	4.15:1.39	20	16	"	80.5	(1)(8)
4	4.98:1.0	0	8	"	75.8	(1)(8)
5	4.98:1.39	0	9	"	88.5	(1)(8)
6	4.98:1.39	10	10	"	88.5	(1)(8)
7	4.98:1.0	20	14	"	64.6	(1)(8)
8	4.98:1.39	20	17	"	81.3	(1)(8)
9	5.81:1.0	20	13	"	54.4	(1)(8)
10	5.81:1.39	20	15	"	70.2	(1)(8)
V 1	3.74:1.0	10	10	60	75.6	(2)(9)
2	3.74:1.1	"	13	"	79.7	(2)(9)
3	3.74:1.2	"	13	"	82.4	(2)(9)
4	3.74:1.2	"	11	"	86.9	(2)(9)
5	3.74:1.3	"	14	30	88.0	(2)(9)
6	3.74:1.3	"	16	60	86.6	(2)(9)
7	3.74:1.3	"	12	90	83.9	(2)(9)
8	3.74:1.4	"	12	15	91.4	(2)(9)
9	3.74:1.4	"	13	30	88.5	(2)(9)
10	3.74:1.4	"	9	45	90.2	(2)(9)
11	3.74:1.4	"	14	45	90.3	(2)(9)
12	3.74:1.4	"	14	60	90.4	(2)(9)
13	3.74:1.4	"	13	60	90.1	(2)(9)
14	3.74:1.4	"	17	90	86.8	(2)(9)
15	3.74:1.5	"	13	45	90.7	(2)(9)
16	3.74:1.5	"	12	60	91.0	(2)(9)
17	3.74:1.6	"	14	45	92.0	(2)(9)
18	3.74:1.7	"	13	45	92.0	(2)(9)
19	3.74:1.8	"	14	45	91.2	(2)(9)

Note reference

(1) Water used for washing nitroguanidine precipitated from nitration mixture.

(2) A saturated solution (at room temperature, ca. 20°C.) of nitroguanidine used for washing nitroguanidine precipitated from nitration mixture, to minimise solubility losses.

(3) Guanidinium hydrogen sulphate, $GuHSO_4$, dissolved in concentrated sulphuric acid without cooling; temperature reached ca. 55°C. Solution was cooled prior to addition of nitric acid.

(4) Frothing in these experiments, Series I, was somewhat marked during period of stirring.

(5) The solution of $GuHSO_4$ in concentrated sulphuric acid was heated successively at 60°C. (1 hour), 80°C. (1 hour) and 100°C. (1 hour) prior to addition of nitric acid. No change in guanidine content was observed during the period of heating.

(6) $GuHSO_4$ dissolved in concentrated H_2SO_4 keeping temperature below 30°C., then added nitric acid.

(7) In Series III the solution of $GuHSO_4$ in concentrated H_2SO_4 was heated at 80°C. for 2 hours prior to addition of nitric acid. Earlier experiments appeared to indicate that this treatment reduced the frothing during stirring of nitration mixture.

Frothing was much less troublesome at 0°C. than at 20°C.; good stirring broke down any froth formed. Some nitration mixtures developed, at 20°C., an initial pale green colour which changed to cream yellow. Reaction mixture possessed a faint odour of acetaldehyde.

(8) In Series IV the solution of $GuHSO_4$ in concentrated H_2SO_4 was not heated prior to addition of nitric acid. The use of 1.39 moles HNO_3 per mole guanidine was sufficient to nitrate all unchanged urea, if present, in addition to guanidine.

Frothing occurred in all nitrations; it was easily controlled at 0°C. and 10°C., but only with good stirring at 20°C. At 0°C. no colour developed in nitration mixture; at 10°C. only a faint tinge; at 20°C. a colour change from pale green to pale cream yellow occurred, accompanied by faint odour of acetaldehyde.

(9) In Series V the molar ratio, guanidine : H_2SO_4, 1 : 3.74 is equivalent to the weight ratio, guanidine : H_2SO_4, 1.0 : 6.21 and corresponds to the weight ratio, guanidine nitrate : H_2SO_4, 1 : 3, which has ordinarily been used for the large scale preparation of nitroguanidine. A temperature of nitration was chosen at 10°C. to minimise frothing, due probably to degradation of unstable nitramine impurities; also, to limit oxidation of impurities present in solution of $GuHSO_4$.

In all nitrations at 10°C. some slight frothing occurred the nitration mixture passing through a pale green coloration to very pale yellow. Nitration mixture was slightly exothermic in behaviour, i.e. tended to liberate some heat on continued stirring, due to the incidence of a degradation reaction. All reaction mixtures possessed an odour of acetaldehyde and in one instance a trace of ethyl nitrate was detected.

When using nitric acid ratios greater than 1.4 mole per mole guanidine

some frothing occurred in the drowned reaction mixture. The waste acid in these cases was somewhat yellow in colour and some slight oxidative reaction appeared to occur in the drowned liquor on standing.

Composition of Waste Acid

Waste acid from nitration study was subjected to a number of analyses to determine the approximate composition.

Typical analyses are shown below:

Composition	Waste Acid Series V, 11 %	Waste Acid Series V, 13 %
Total acidity, as H_2SO_4	17.52	18.28
Total SO_4 ion, as H_2SO_4	18.22	18.79
Free H_2SO_4	16.89	17.63
Free HNO_3	nil	nil
Fixed HNO_3, as $-N.NO_2$	0.66	0.81
Bases as $(NH_4)_2SO_4$ (a)	1.13	1.84
Bases as $(NH_4)_2SO_4$ (b)	1.02	1.07
Potential N as $(NH_4)_2SO_4$	2.77	2.90
Total Nitrogen	0.59	0.61
Weak acid as CO_2	0.08	0.09
Reducing material as HNO_2	0.06	0.02
Water (approx.) calculated	77.29	77.38

(a) By expulsion of volatile bases by use of standard alkali.

(b) By the formaldehyde method of Grisson (6).

Concentration of Waste Acid

No detailed study of the concentration of waste acid has as yet been made. The calculated composition of the concentrated acid, assuming no loss of sulphate ion as sulphur dioxide during concentration, is approximately: H_2SO_4, 35.1; $(NH_4)_2SO_4$, 14.8 per cent. Kendall and Landon (7) have shown that this system has a freezing point of ca. -13°C.

Conclusion: It is concluded from the investigation that the optimum conditions for the nitration of guanidinium hydrogen sulphate, prepared as described heretofore, are:

(i) Use of the molar ratio, Guanidine : H_2SO_4 : HNO_3, 1 : 3.74 : 1.4. The molar ratio, Guanidine : H_2SO_4 is equivalent to that which obtains using the weight ratio, Guanidine nitrate : H_2SO_4, 1 : 3, which has ordinarily been used in the production of nitroguanidine. The molar ratio, Guanidine : HNO_3, is however greater than that, viz. 1 : 1, used in the production of nitroguanidine. The excess, viz. 0.4 mole HNO_3, is essential owing to the incidence of side reactions, that is, the nitration of impurities of amine type structure which are present in the original material; no free nitric acid is present in the waste acid.

(ii) Nitration at a temperature of 10°C. for a period of 30 mins. The conversion of guanidine to nitroguanidine in the medium H_2SO_4-HNO_3 is relatively rapid even at low temperatures (8). The rate and extent of conversion are

however determined 'inter alia' by the nature and concentration of impurities. Since, in this case, the solution of $GuHSO_4$ contains impurities of amine type structure these give nitramine derivatives on nitration which are not stable and tend to degrade. This degradation is the more rapid the higher the nitration temperature and tends to form a froth which is negligible at 10°C. but may be troublesome on the large scale in the range 10°C.-30°C. Again an oxidative reaction occurs during nitration involving the ethyl group; the ethyl group is present in the original material either as unrecovered alcohol in the distillation stage, or, an impurity such as $EtHSO_4$ which would give alcohol under the working conditions.

Further investigation of the nitration stage is necessary at more elevated temperatures, e.g. 20°C. and 30°C., with the object of reducing the time interval for complete nitration in a continuous nitration process.

Finally, any improvements introduced at the earlier stages of ethylation, amination and hydrolysis will be reflected in the purity of guanidinium hydrogen sulphate which may therefore require modification of the conditions of nitration.

11. Purification of Nitroguanidine

All samples of crude nitroguanidine obtained in the nitration study (this report, section 10) showed melting points in the range 235-238°C., with decomposition.

The crude material is purified by recrystallisation from water. No apparent degradation was observed and the hot solution was clear, showing absence of insoluble impurities, and colourless. However, a corrected loss of 3-4 per cent was noted on recrystallisation.

A sample of recrystallised material was submitted to the specification tests for service grade material, and satisfied all tests.

The Infra Red spectra, of a sample of recrystallised nitroguanidine, prepared from urea, and a sample of recrystallised nitroguanidine, prepared from guanidine nitrate derived from calcium cyanamide, were compared under the same conditions. The spectra were identical indicating that both samples were of strictly comparable purity.

12. A process for the production of nitroguanidine (picrite) from urea

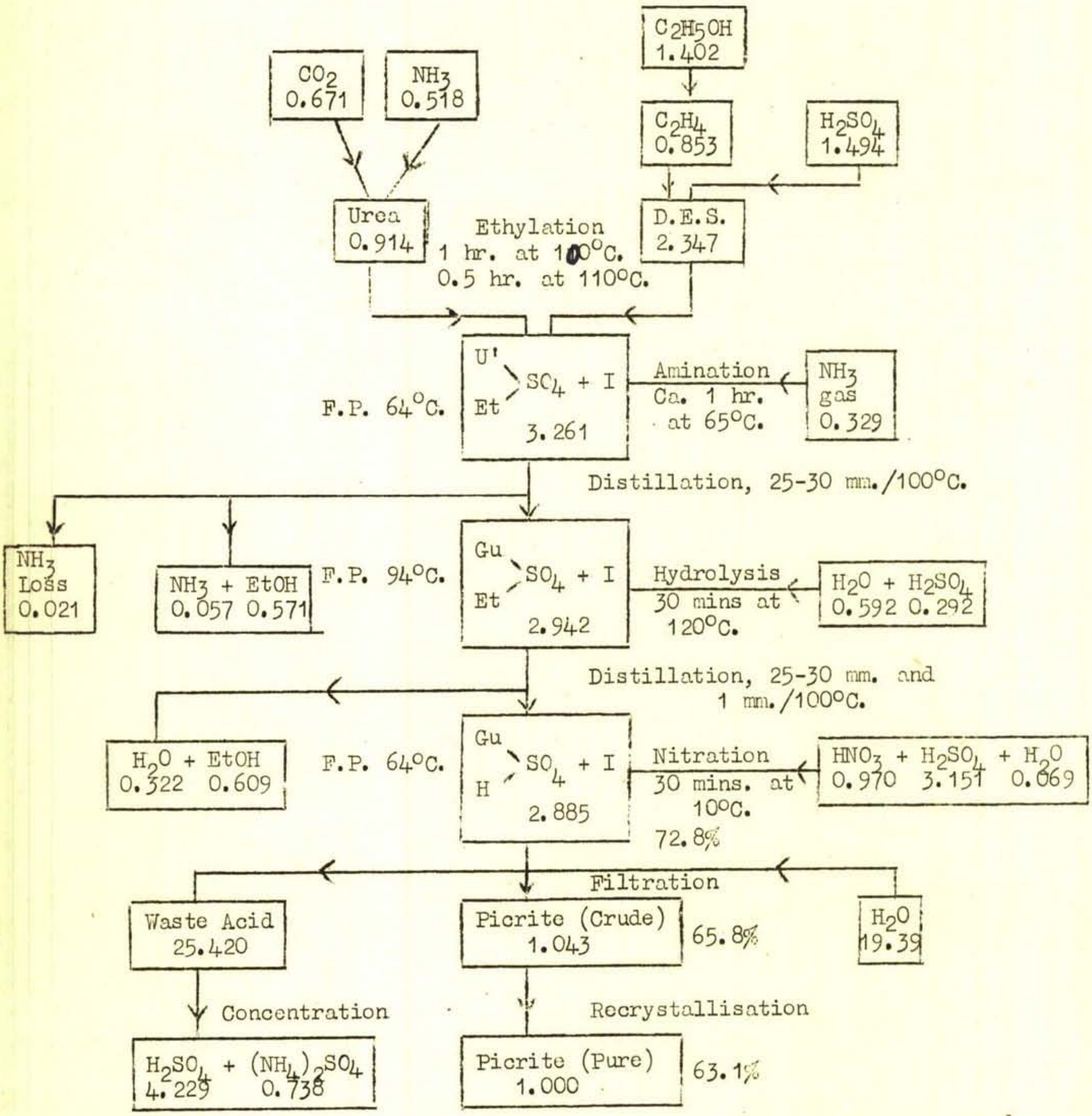
On the basis of the studies respecting the stages of alkylation, amination, hydrolysis and nitration described heretofore a process for the production of nitroguanidine from urea has been developed.

A typical flowsheet for the projected process is given below. The experimental data which form the basis of the materials data are contained in the 'Experimental' part (this report, Section 25, Exp.IV, and Section 26, Tables X and XI, Exp. 13).

Flowsheet

Molar Ratio Urea : Di-ethyl Sulphate (D.E.S.) = 1:1

Parts per part pure picrite



(i) Per cent values in table show the overall yield at each stage based on urea.

(ii) U' = $\left[C \begin{matrix} NH_2 \\ - OEt \\ NH_2 \end{matrix} \right]^+$; Gu ≡ $\left[C \begin{matrix} NH_2 \\ - NH_2 \\ NH_2 \end{matrix} \right]^+$; I ≡ Other products

(iii) Material quantities for production of urea and D.E.S. are theoretical.

Typical Analyses

	Parts/part pure picrite	
$Gu\,H > SO_4$ + I (other products)	2.885	
Bases as $(NH_4)_2SO_4$	0.215	
Guanidine	0.655	
H_2SO_4 free Gu_2SO_4	0.898	
H_2SO_4 fixed as $GuSO_4$	0.544	
Potential N_2 as $(NH_4)_2SO_4$	2.876	
Waste acid	25.420	%
Total acid as H_2SO_4	4.648	18.28
Total SO_4 ion as H_2SO_4	4.777	18.79
Free H_2SO_4	4.481	17.63
Free HNO_3	nil	nil
Fixed HNO_3 as $-N.NO_2$	0.205	0.81
Bases as $(NH_4)_2SO_4$	C.272	1.07
Potential N_2 as $(NH_4)_2SO_4$	0.738	2.90
Weak acid as CO_2	0.022	0.09
Reducing material as HNO_2	0.019	0.08
Water (calculated)	19.67	77.38
Concentrated Waste Acid		%
H_2SO_4, theory	4.229	85.13
$(NH_4)_2SO_4$, theory	0.738	14.85

Materials Balance

	Parts/part pure picrite
H_2SO_4 for Et_2SO_4	1.494
H_2SO_4 for Hydrolysis	0.292
H_2SO_4 for Nitration	3.151
∴ Total input of H_2SO_4	4.937
H_2SO_4 recovered in Waste Acid	4.229
∴ Consumption of H_2SO_4	0.708
EtOH for Et_2SO_4	1.402
EtOH recovered from amination	0.571
EtOH recovered from hydrolysis	0.609
Total EtOH recovered	1.180
∴ Consumption of EtOH	0.222
NH_3 consumed at amination	0.251
NH_3 required for urea	0.518
∴ Consumption of NH_3	0.769
CO_2 required for urea	0.671
∴ Consumption of CO_2	0.671
Consumption of HNO_3	0.970

Significant features of the process

Some characteristics of the projected process are:

(1) All stages of the process can be carried out in one vessel, i.e. in the laboratory.

In practice all operations can be conducted continuously. At all stages the reaction mixture is kept in the liquid state.

(2) The whole process is self-contained.

The diethyl sulphate used in the process is an intermediate in one mode of production of ethyl alcohol on the large scale. It is used efficiently in the process. The overall recovery, as ethyl alcohol, of the ethyl groups in diethyl sulphate is of the order of 85 per cent theory. The recovered alcohol (ca. 40 per cent of total), at the amination stage is anhydrous and at the hydrolysis stage ca. 42 per cent of total, has an overall concentration of ca. 65 per cent (by weight); the latter can readily be dehydrated for further use. The recovered alcohol can either be recycled or replaced by fresh ethylene; the recycle of alcohol need not necessarily be via ethylene since a recent process (9) has been developed for the direct conversion of ethyl alcohol, by treatment with concentrated sulphuric acid, into diethyl sulphate in 90 per cent yield. The sulphate radical of the diethyl sulphate is usefully employed at the nitration stage. At the end of the hydrolysis stage 77 per cent of the sulphate radical is distributed as free acid and fixed as guanidine sulphate; the remainder is fixed as neutral salts of base impurities.

The ammonia required at the amination stage is almost theory; the slight excess used can be recycled.

At the nitration stage the molar ratio, Gu : H_2SO_4 : HNO_3, 1 : 3.74 : 1.4, has been used; this ratio represents the optimum. The ratio Gu : H_2SO_4 is equivalent to that used for the weight ratio $GuHNO_3$: H_2SO_4, 1 : 3, which has ordinarily been used in the production of nitroguanidine on the large scale. The slight excess of nitric acid, viz. 0.4 mole, used is essential for the side nitration of impurities; no free nitric acid appears in the waste acid.

The yield of pure picrite, viz. 63 per cent based on urea, compares very favourably with that obtained, ca. 54 per cent based on nitrolim assumed to contain 65 per cent calcium cyanamide or 74 per cent based on dicyandiamide, heretofore by the Welland process.

The disposal of the waste acid is the major problem; this can after reconcentration either be (a) integrated into the chemical industry; this point is considered below, (b) used in part for the preparation of diethyl sulphate, and (c) possibly used in part again in the nitration stage.

(3) The energy changes involved are low, and the plant and process costs should be relatively low.

(4) The process in essence is reduced to the commonest denominator, viz. simplicity.

(5) So far the elements of the process have been established. It remains to examine each stage of the process again more critically in order to define exact operating conditions for a continuous process.

(6) Finally, it remains to assess the process on an economic basis.

13. Sulphuric Acid. Consumption in the United Kingdom

The disposal of waste acid containing all the sulphuric acid used in the nitration stage in the production of nitroguanidine is a major problem. In the process outlined above (Section 12) the relative amounts, in concentrated waste acid, are H_2SO_4, 4.23 parts and $(NH_4)_2SO_4$, 0.74 part. A high production of nitroguanidine accentuates the waste acid disposal problem and it is imperative that it be usefully conserved. Indeed, the high annual consumption of sulphur in the form of sulphuric acid in the U.K., U.S.A., and other countries is a matter of concern which will be greater in course of time. Thus it is of vital importance to effect economy wherever possible in the usage of sulphuric acid. The primary ideal in this case under consideration is its recycle for use wherever possible, e.g. in the preparation of diethyl sulphate and nitration stage, and secondarily its integration into the chemical industry.

The following is a summary (10) of sulphuric acid and oleum consumption in the U.K. and Southern Ireland during the second quarter, April 1 - June 30, 1949.

(In terms of 100 per cent H_2SO_4)

Uses	Tons
Accumulators	2,197
Agricultural Purposes	1,736
Bichromate and Chromic Acid	2,909
Bromine	2,941
Clays (Fullers Earth, etc.)	2,048
Copper Pickling	666
Dealers	4,267
Drugs and Fine Chemicals	2,552
Dyestuffs and Intermediates	17,046
Explosives	2,884
Export	804
Glue, Gelatine and Size	536
Hydrochloric Acid	15,795
Iron Pickling (incl. Tin Plate)	22,505
Leather	1,536
Metal Extraction	556
Oil (Mineral) Refining	14,476
Oil (Vegetable) Refining	2,601
Paint and Lithophone	27,406
Paper etc.	1,089
Phosphates (Industrial)	1,314
Plastics, not otherwise classified	3,919
Rayon and Transparent Paper	39.401
Sewage	2,744
Soap and Glycerine	1,524
Sugar Refining	163
Sulphate of Ammonia	62,386
Sulphate of Barium	1,287
Sulphate of Copper	5,313
Sulphate of Magnesium	1,478
Sulphate of Zinc	805
Superphosphates	130,329
Tar and Benzole	4,383
Textile Uses	5,872
Unclassified Uses Known*	23,598
Uses unknown	11,010
Total	422,076

* Boric acid, Borax, Chlorosulphuric acid, Formic acid, hydrofluoric acid, Oxalic acid, nitric acid, tartaric acid, Rare Earths, Aluminium sulphate.

The following is an extract from the 'Report of the Minerals Development Committee' (11).

Anhydrite

"Resources of anhydrite in the Billingham area are likely to be at least 75 m. tons. Further large resources exist south of the River Tees. Many millions of tons of anhydrite are also known to be present in the Eden Valley in Cumberland and Westmorcland also in West Cumberland. It is clear that the resources are sufficient to meet requirements on present day standards for many years. Production in 1947 was 919,825 tons of which 828,021 tons was at Billingham. Consumption in 1947 was 880,060 tons of which 717,321 tons for ammonium sulphate (≡ 653,000 tons $(NH_4)_2SO_4$) and 154,892 tons for sulphuric acid."

Comment. The waste acid in the process discussed heretofore (Section 12) after concentration corresponds approximately to 4.229 parts H_2SO_4 and 0.738 parts $(NH_4)_2SO_4$ per part picrite.

For an output of 1100 tons picrite per week the quantities of H_2SO_4 and $(NH_4)_2SO_4$ in the waste acid would be 241,800 tons and 42,220 tons per annum respectively. This quantity of H_2SO_4 corresponds to ca. 14 per cent of the total quantity consumed in the United Kingdom. The quantity of $(NH_4)_2SO_4$ corresponds to ca. 6.5 per cent of the total quantity prepared from anhydrite in 1947. If all the waste acid were to be converted to $(NH_4)_2SO_4$ the total annual output, i.e. for 1100 tons picrite per week, would be 367,900 tons corresponding to ca. 56 per cent of the total quantity prepared from anhydrite in 1947.

The presence of ammonium sulphate, and/or traces of base sulphate impurities, in concentrated waste acid would perhaps not be deleterious in some industrial applications. These applications have been tabulated above; it is worthy of note that the annual H_2SO_4 requirements are for superphosphates, 521,000 tons, $(NH_4)_2SO_4$ (i.e. direct from H_2SO_4), 249,000 tons (≡ 335,500 tons $(NH_4)_2SO_4$) and iron pickling 89,000 tons.

In general the basic idea relating to the process under review is to utilise sulphuric acid, prepared primarily from imported sulphur and sulphur ores, in the preparation of diethyl sulphate and at the nitration stage, and route the recovered acid from the process into useful industrial channels. Thus, greater efficiency in the usage of the original sulphuric acid would be attained.

These considerations suffice to indicate how the waste acid could be integrated into the chemical industry.

14. Conclusion

The elements of a process for the production of nitroguanidine (picrite), based on urea, have been established. One of the main features of the process is the utilisation of diethyl sulphate for the alkylation of urea and subsequent recovery of the ethyl groups as alcohol and the sulphate radical as free sulphuric acid which can be usefully employed in the process. The yield, based on urea, of nitroguanidine, of satisfactory purity, is ca. 63 per cent; this compares favourably with that, viz. 54 per cent based on nitrolim, obtained in the Welland process.

15. Recommendations

(i) A more critical examination is warranted of each stage in the proposed

process for the production of nitroguanidine from urea in order to introduce possible improvements and define more exact conditions for a continuous technical process.

(ii) A preliminary economic assessment of the process should be made for its evaluation relative to any other alternative route to nitroguanidine.

and, (iii) A comprehensive study of the chemical changes involved at the various stages in the process should be carried out in order to define the character of by-products.

16. Acknowledgments

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EXPERIMENTAL

18. Alkylation of Urea with Diethyl Sulphate and the conversion of O-Ethyl-isourea to Guanidine

The experiments now described are a continuation of those, Series I, recorded (Section 23) in a previous report (2). These were carried out to determine the optimum conditions for the conversion of urea to O-ethyl-isourea.

General Method

Diethyl sulphate (Laboratory grade material; purity 99.8 per cent, acidity $<$ 0.5 per cent as H_2SO_4), varying quantities, were introduced at ordinary temperature into a boiling tube fitted with a mechanical stirrer and thermometer. The mixture was heated with good stirring to the required reaction temperature and there maintained for varying periods. In each case the time which elapsed before the reaction mixture became clear and homogeneous was observed. The reaction mixture was then cooled, diluted with water and made up to a volume of 100 ml.

The solution was analysed for total acidity and O-ethyl-isourea, indirectly by conversion to guanidine.

Total acidity

Aliquot portions, 10 ml., were titrated with N/1 sodium hydroxide using methyl red as indicator.

O-ethyl-isourea

A portion, 50 ml., of the solution was first neutralised with 0.880 ammonia, and then treated with sufficient concentrated (0.880) ammonia to give 1.2 moles ammonia per mole urea used. The solution was heated in a stoppered flask for 3 hours at 60°C., then cooled, diluted with water and made up to 100 ml. Portions, 5 ml., of the solution were analysed for guanidine by the method previously described (1).

Series II. The effect of varying the molar ratio urea : diethyl sulphate, keeping all other conditions constant, on the yield of O-ethyl-isourea

The experimental conditions together with the analytical data are given in Table I.

Table I

Diethyl sulphate (D.E.S.) used, 12.83 g. (1 mol.).

Urea used, 4 g. to 10 g. (0.8 mol. to 2.0 mols.).

Reactants mixed at ordinary temperature and heated with stirring at 100°C. for 60 mins. (Note: Previous work (2) had shown that alkylation was complete under these conditions using the molar ratio, urea : D.E.S., 1 : 1).

UREA		Time for R.M. ※ to clear Mins.	ACIDITY AS $EtHSO_4$		GUANIDINE		
g.	Moles Per Mole D.E.S.		g.	% on D.E.S.	g.	% on Urea	% on D.E.S.
4.0	0.8	10	0.937	8.92	2.92	74.16	59.33
4.5	0.9	9	1.267	12.06	3.21	72.47	65.22
5.0	1.0	9	1.034	9.85	3.53	71.80	71.80
5.5	1.1	8	1.034	9.85	3.87	71.45	78.59
6.0	1.2	8	0.814	7.75	3.94	66.73	80.07
7.5	1.5	7	0.595	5.66	3.96	53.68	80.52
10.0	2.0	6	0.194	1.85	3.95	40.20	80.39

※ R.M. = Reaction mixture

The results, Table I, indicate the molar ratio urea : diethyl sulphate, 1.2 : 1.0, to be the most economical, on the assumption that diethyl sulphate is the more costly reactant. This ratio was therefore chosen for the next series (III) of experiments.

Series III The effect of varying the temperature and time of reaction using the molar ratio, urea : diethyl sulphate, 1.2 : 1.0, on the yield of O-ethyl-isourea

The experimental conditions together with the analytical data are given in Table II.

Table II

Diethyl sulphate (D.E.S.) used, 12.83 g. (1.0 mol.)

Urea used, 6.0 g. (1.2 mol.)

Reaction Temp. °C.	Time Total mins.	Time To clear mins.	Acidity as $EtHSO_4$ g.	Acidity as $EtHSO_4$ % on D.E.S.	Guanidine g.	Guanidine % on Urea	Guanidine % on D.E.S.
80	90	60	2.042	19.45	3.55	60.12	72.14
"	120	55	1.357	12.92	3.69	62.52	75.02
"	150	62	1.357	12.92	3.79	64.19	77.03
"	180	53	1.357	12.92	3.83	64.94	77.93
90	30	23	1.227	11.69	3.16	53.56	64.25
"	60	22	1.260	12.00	3.76	63.74	76.49
"	90	24	1.227	11.69	3.91	66.21	79.45
"	120	25	1.150	10.95	3.95	66.91	80.30
100	30	8	1.176	11.20	3.79	64.27	77.13
"	60	8	0.982	9.35	3.95	66.97	80.37
"	90	7	0.530	5.05	3.91	66.34	79.62
110	15	3	0.969	9.23	3.91	66.34	79.62
"	30	3	0.646	6.16	3.95	67.01	80.41
"	60	3	0.129	1.23	3.90	66.18	79.41
120	5	1	0.937	8.92	3.81	64.63	77.56
"	10	1	0.659	6.28	3.90	66.07	79.29
"	15	1	0.258	2.46	3.90	66.06	79.27

The results, Table II, indicate that the ethylation of urea is optimum after 2 hours at 90°C., 1 hour at 100°C., or 0.5 hour at 110°C. In practice it is preferred to operate at 100°C. or 110°C.

At a later stage of the work it was considered desirable to carry out a similar series of experiments using the molar ratio, urea : diethyl sulphate, 1.0 : 1.0. This ratio was therefore chosen for the next series (IV) of experiments.

Series IV. The effect of varying the temperature and time of reaction using the molar ratio, urea : diethyl sulphate, 1.0 : 1.0 on the yield of O-ethyl-isourea

The experimental conditions together with the analytical data are given in Table III.

Table III

Urea used, 5.0 g. (1 mol.)

Diethyl sulphate (D.E.S.) used, 12.83 g. (1 mol.)

Reaction Temp. °C.	Time		Acidity as $EtHSO_4$		Guanidine	
	Total mins.	To clear mins.	g.	% on D.E.S.	g.	% of Theory
100	15	9	1.26	12.00	2.97	60.4
"	30	9	1.29	12.25	3.23	65.6
"	60	9	1.22	11.63	3.43	69.7
"	90	10	1.16	11.03	3.56	72.3
110	15	4	1.24	11.76	3.34	67.9
"	30	4	1.03	9.80	3.49	71.1
"	45	4	0.78	7.47	3.47	70.6
"	60	4	0.76	7.23	3.52	71.5
120	5	1	1.04	9.92	3.22	65.4
"	10	1	0.93	8.82	3.41	69.3
"	15	1	0.71	6.74	3.43	69.7
"	20	1	0.58	5.51	3.46	70.4

Series V   The effect of the addition of pyridine in the alkylation of urea using diethyl sulphate

In experiments (see below) on the amination of reaction mixtures containing O-ethyl-isourea with gaseous ammonia it was found that no ammonia was absorbed corresponding to the titratable acidity of the reaction mixture. It was considered that this acidity might be due to the pressure of an urea salt in the reaction mixture and, as it had already been shown (2) that salts of urea do not react with alkyl sulphates, this might account for the low yields obtained at the alkylation stage. Accordingly some alkylation experiments were carried out with addition of pyridine to take up free acidity in place of urea. The method of experiment was almost identical with that described above. The requisite amount of pyridine was added to the diethyl sulphate when a turbid mixture was obtained which soon became clear with evolution of heat. The urea was then added and the alkylation effected as previously described.

Parallel experiments were carried out without the addition of pyridine.

The experimental conditions together with the analytical data are given in table IV.

Table IV

Urea used, 5.0 g. (1 mol.)

Diethyl sulphate (D.E.S.) used, 12.83 g. (1 mol.)

Reaction Temp. °C.	Moles Pyridine	Time		Acidity as $EtHSO_4$		Guanidine	
	Per Mole D.E.S.	Total mins.	To clear mins.	g.	% on D.E.S.	g.	% of Theory
100	-	30	9	1.29	12.25	3.23	65.7
100	0.05	30	6	1.18	11.27	3.30	67.1
110	-	30	4	1.03	9.80	3.49	71.1
110	0.10	30	1	0.80	7.60	3.39	69.0

19. Heat Evolution in the reaction between Urea and Diethyl Sulphate

Experiments were carried out to observe the extent of heat evolution during the ethylation of urea with diethyl sulphate, using molar ratio 1 : 1, and the maximum temperature likely to be attained if the temperature of a reaction mixture were not controlled.

Series I

Diethyl sulphate (12.83 g.) and urea (5.0 g.) were mixed in a boiling tube fitted with a stirrer and thermometer. The tube was immersed in an air bath maintained at 100°C. and the increase in temperature with time of the well stirred reaction mixture was observed.

Initially there was a steady rise until about 94°C. was reached and then the temperature remained almost steady for several minutes while the urea melted. As soon as the reaction mixture was all fluid there was a steadily accelerated rise in temperature, the mixture becoming clear and homogeneous when a temperature of about 115°C. was attained.

When the temperature reached 120°C. it was controlled, some cooling being necessary. Heating was later applied as necessary to maintain the temperature of the reaction mixture at 120°C. for a total period of 15 mins.

The mixture was cooled, and analysed for acidity and O-ethyl-isourea, indirectly by conversion to guanidine, in the usual way.

Duplicate experiments were carried out.

Experimental data are tabulated below:

Time Mins.	Temp. of R.M. °C.		Time	Temp. of R.M. °C.	
	Expt. 1	Expt. 2	Mins.	Expt. 1	Expt. 2
0	-	-	9.0	94.7	94.1
2.5	77.2	75.0	9.5	95.0	94.3
3.0	81.0	-	10.0	95.5	94.4
3.5	84.3	82.3	10.5	95.9	94.7
4.0	86.9	85.2	11.0	96.5	95.0
4.5	88.7	87.5	11.5	97.3	95.7
5.0	90.1	89.2	12.0	98.1	96.4
5.5	91.1	90.5	12.5	99.0	97.2
6.0	92.2	91.4	13.0	100.6	98.1
6.5	93.0	92.1	13.5	103.7	99.3
7.0	93.6	92.6	14.0	109.0	100.8
7.5	94.0	92.9	14.5	*115.6C	103.9
8.0	94.3	93.4	15.0	-	109.0
8.5	94.6	93.9	15.5	-	*115.4C

* R.M. = Reaction mixture

C=R.M. became clear and homogeneous

Expt.	Acidity as $EtHSO_4$		Guanidine	
	g.	% on D.E.S.	g.	% of Theory
1	0.84	7.96	3.48	70.8
2	0.86	8.21	3.42	69.5

Series II

The reaction was carried out as described in Series I but no attempt was made to control the temperature. It was found that a maximum temperature of 124°C. was attained after which the temperature of the mixture fell rapidly. Observations were continued until the temperature of the reaction mixture had again reached 100°C. The material was then cooled and the usual analyses carried out.

Experimental data are tabulated below.

From the temperature values obtained it would seem unlikely that any danger exists of the reaction going completely out of control. Further, the alkylation is not apparently complete under the time-temperature conditions investigated.

Time Mins.	Temp. of R.M. °C. Expt. 1	Temp. of R.M. °C. Expt. 2	Time Mins.	Temp. of R.M. °C. Expt. 1	Temp. of R.M. °C. Expt. 2
0	-	-	12.0	99.9	99.1
2.0	-	76.5	12.5	102.3	101.1
2.5	80.1	81.4	13.0	107.0	105.0
3.0	83.8	84.5	13.5	113.9C	110.5
3.5	86.5	87.0	14.0	-	116.0C
4.0	88.2	89.1	14.5	123.8	119.9
4.5	90.1	90.3	15.0	121.0	119.6
5.0	91.7	91.5	15.5	117.2	117.3
5.5	92.9	92.2	16.0	114.5	114.3
6.0	93.7	92.9	16.5	112.2	111.4
6.5	94.2	93.5	17.0	110.3	109.2
7.0	94.5	94.0	17.5	108.4	107.2
7.5	94.8	94.3	18.0	106.7	105.3
8.0	95.2	94.7	18.5	105.1	103.8
8.5	95.6	94.8	19.0	103.6	102.8
9.0	96.0	95.0	19.5	102.2	102.1
9.5	96.4	95.2	20.0	100.9	101.5
10.0	96.7	95.4	20.5	100.4	100.9
10.5	97.2	95.9	21.0	-	100.4
11.0	97.7	96.6	21.5	-	99.8
11.5	98.6	97.8			

Expt.	Acidity as $EtHSO_4$ g.	Acidity as $EtHSO_4$ % on D.E.S.	Guanidine g.	Guanidine % of Theory
1	1.16	11.03	3.26	66.3
2	1.16	11.03	3.23	65.8

20. Alkylation of Urea using Di-isopropyl sulphate

Di-isopropyl sulphate. This material was supplied by the Distillers Company Ltd. The material, purity 93 per cent, as received was a dark coloured oil. It was deacidified and dried by standing over anhydrous potassium carbonate.

A portion of the dried material was filtered and distilled in vacuo. A small portion of colourless distillate was obtained but a vigorous decomposition set in with evolution of gas, propylene, during the distillation which was then discontinued. The residue was dark coloured and strongly acid. The distillate, B.P. 76°C./2 mm., soon developed a purple colour on standing and is unstable at ordinary temperatures; it develops an acidity which progressively increases on storage.

Alkylation of urea was carried out using the redistilled ester and also the diacidified crude material.

(i) Alkylation using redistilled Di-isopropyl sulphate

Quantities used:

Urea	5.0 g.	(1 mol.)
Di-isopropyl sulphate	15.17 g.	(1 mol.)

Above materials were mixed and reacted at 100°C. in the usual way. Considerable gas evolution occurred and material which was initially colourless soon became dark reddish purple in colour.

The mixture became homogeneous in 10-15 mins. Heating at 100°C. was continued to give a total reaction period of 1 hour. Reaction mixture was cooled, dissolved in water and made up to a volume of 100 ml. when about 0.5 ml. of oil separated; this oil was not examined.

Total acidity was determined on an aliquot portion of solution. Another portion was aminated as previously described and the guanidine estimated; this also gives indirectly a measure of the alkylation.

Found: Total acidity as Pr HSO_4 = 30 per cent on Pr_2SO_4.

Guanidine = 2.19 g. ≡ 44.6 per cent on urea.

(ii) Alkylation using crude Di-isopropyl sulphate

Quantities used:

Urea 5.0 g. (1 mol.)
Di-isopropyl sulphate (purity 93 per cent), 16.31 g. (1 mol.)

Note: Owing to the instability of di-isopropyl sulphate and the low yields of guanidine obtained no further work with this ester was attempted.

21. Attempts to alkylate urea directly by use of ethylene and isobutylene

A. Use of Ethylene

(i) Quantities used:

Urea	60 g.	(1 mol.)
Diethyl sulphate	154.0 g.	(1 mol.)

The ethylation using above materials was carried out in the usual way, a rapid stream of ethylene being passed through the mixture during the entire reaction period.

Temperature of reaction	100°C.
Time for reaction mixture to clear	8 mins.
Total reaction time	60 "
Weight of final reaction mixture	212.6 g.
Loss in weight	1.4 g.

No absorption of ethylene occurred under these conditions.

A portion of the mixture was examined for acidity and guanidine, after amination, in the usual way.

Found:

Total acidity, as H_2SO_4 = 5.55 g.

Total guanidine = 40.61 g.

≡ 68.84 per cent on ethyl sulphate.

(ii) To the bulk of material, final reaction mixture from (i), was added a further quantity of urea. The mixture was heated to 100°C. when a

clear liquid was obtained. This liquid was well stirred at 100°C. whilst sulphuric acid equivalent to the urea was slowly dripped in and a rapid current of ethylene passed through the reaction mixture.

Weight of reaction mixture from (i)	203.8 g.
Urea	29.6 g. (0.5 mol.)
Sulphuric acid (98.1%)	47.4 g. (0.5 mol.)
Temp. of reaction	100°C.
Time of addition of H_2SO_4	69 mins.
Ethylene passed in for	30 mins.
Weight of final reaction mixture	278.1 g.
Loss in weight	2.7 g.

Apparently no absorption of ethylene occurs under these circumstances.

The final reaction mixture was a brownish viscous liquid which crystallised on standing to give a solid of F.P. 42°C.

A portion of this material was analysed for total acidity and guanidine after amination.

Total acidity, as H_2SO_4	45.76 g.
Total acid, as H_2SO_4, in original mixture from (i)	5.32 g.
H_2SO_4, 100%, added in (ii)	46.50 g.
Total acid added	51.82 g.
Loss of H_2SO_4	6.06 g.

If the reaction $CO\begin{smallmatrix}\diagup NH_2\\ \diagdown NH_2\end{smallmatrix} + H_2SO_4 + H_2O \rightarrow (NH_4)_2SO_4 + CO_2$ be considered.

Loss of 6.06 grams H_2SO_4 = liberation of 2.72 g. CO_2.
c.f. observed loss in weight of 2.70 g.

Total guanidine from (ii)	45.63 g.
Total guanidine from (i) added to (ii)	38.94 g.
Increase in guanidine	6.69 g.

≡ 11.82 per cent on diethyl sulphate in material from (i)

Urea added in (ii) = 0.52 mole per mole diethyl sulphate used in (ii) from (i).

In (i) using mol. ratio urea : diethyl sulphate, 1 : 1; yield of guanidine = 68.84 per cent.

In (ii) using mol. ratio urea : diethyl sulphate, 1.52 : 1, yield of guanidine = 80.66 per cent.

Previous experimental work, section 17, showed that yields of guanidine using mol. ratios 1 : 1 and 1.5 : 1 are 71.8 per cent and 80.4 per cent respectively. It therefore seems probable that the increased yield of guanidine is due solely to the addition of further urea to the reaction mixture and not to any consumption of ethylene.

B. Use of Isobutylene

Experiments similar to those described under (A), using ethylene, were carried out using isobutylene.

(i) Quantities used:

Urea	60.0 g.	(1 mol.)
Diethyl sulphate	154.0 g.	(1 mol.)

The ethylation using above materials was carried out in the usual way, a rapid stream of isobutylene being passed through the mixture during the entire reaction period.

Temperature of reaction	100°C.
Time for reaction mixture to clear	8 mins.
Total reaction time	60 mins.
Weight of final reaction mixture	214.0 g.
Loss in weight	nil.

With passage of isobutylene no change in appearance in the reaction mixture occurred.

A portion of the mixture was analysed for total acidity and, after amination, guanidine.

Found: Total acidity, as H_2SO_4 = 6.05 g.

Total guanidine = 40.23 g.

= 68.17 per cent on D.E.S.

(ii) To the bulk of the material, final reaction mixture from (i) was added a further quantity of urea. The mixture was heated to 100°C. when a clear liquid was obtained. This liquid was well stirred at 100°C. whilst sulphuric acid equivalent to the urea was added dropwise but slowly and a rapid current of isobutylene passed through the reaction mixture.

Weight of ethylation mixture from (i)	188.8 g.
Weight of urea, added	15.0 g.
Sulphuric acid (98.11%), used	24.7 g.
Time of addition of H_2SO_4	49 mins.
Temperature of reaction	100°C.
Further passage of isobutene	30 mins.
Weight of final reaction mixture	239.6 g.
Increase in weight	11.1 g.

As the addition of sulphuric acid proceeded there was a vigorous reaction when isobutene and sulphuric acid came into contact. The reaction mixture became progressively darker in colour. On cooling the final product was a dark viscous liquid which did not solidify on prolonged standing.

A portion of the mixture was analysed for acidity and, after amination, for guanidine. On dissolving in water the material gave a small quantity of insoluble oil (not tertiary butyl sulphate) which was not removed by heating with aqueous ammonia.

Sulphuric acid, 100%, added in (ii)	24.38 g.
Total acid, as H_2SO_4, in material from (i)	5.34 g.
Total acid, as H_2SO_4, in final reaction mixture	29.68 g.
Increase in acidity, as H_2SO_4	0.11 g.

Apparently no addition of isobutene to sulphuric acid has occurred.

Guanidine in mixture from (i)	35.50 g.
Guanidine in final mixture (ii)	39.19 g.
Increase in guanidine	3.69 g.

= 7.09 per cent on diethyl sulphate

Again the increase in yield of guanidine is not more than would be expected by increasing urea ratio from 1.0 to 1.28 moles per mole diethyl sulphate. The absorption of isobutene is not accompanied by any decrease in acidity. It seems probable that the absorption, as reflected in the increase in weight, is due to polymerisation of isobutene in contact with sulphuric acid.

22. Attempt to prepare Tertiary Butyl Sulphate

Sulphuric acid (98.11 per cent), 234 g., was well stirred and cooled in ice while a slow stream of isobutene was passed into the acid. Absorption of gas was complete with considerable evolution of heat.

Temperature was controlled at 20-25°C. As addition proceeded the reaction mixture became dark orange red in colour.

When 150 g. of isobutene had been absorbed the mixture was allowed to separate. The upper layer was a pale yellow liquid which was drained on to ice and stirred. The product was a clear water white oil, lighter than water. Apparently this material is polyisobutene; it was not investigated further.

The lower layer, 282 g., was almost completely soluble in water. It was analysed for total acid.

Total acid, as H_2SO_4	224 g.
H_2SO_4(100%) used	230 g.

Obviously no addition of isobutene to sulphuric acid occurs under these conditions. The experiment was discontinued.

23. The amination of O-Ethyl-isourea

In our experiments it is understood that amination is conducted using the reaction mixture derived by alkylation of urea using diethyl sulphate. The reaction mixture contains a high percentage, ca. 70-73 per cent, of O-ethyl-isourea as a salt of ethyl hydrogen sulphate and impurities, the exact nature of which are as yet to be investigated.

A. Amination of reaction mixture dissolved in alcohol using gaseous ammonia

(i) Preliminary experiments

Quantities used:

Urea	72 g.	(1.2 mol.)
Diethyl sulphate	154 g.	(1 mol.)

The alkylation of urea, using the above quantities, was effected at 100°C. for 1 hour. The resulting product was dissolved in absolute alcohol and made up to a volume of 500 ml.

Aliquot portions were taken for analysis. The conversion of urea to O-ethyl-isourea was determined indirectly by amination using aqueous ammonia as previously described.

Found: Total acidity, as $EtHSO_4$ $\equiv$ 6.10 per cent on D.E.S.

Total guanidine $\equiv$ 80.61 per cent on D.E.S.

25 ml. of alcoholic solution = 2.355 g. guanidine

25 ml. of the alcoholic ethyl isourea solution was placed in a boiling tube and gaseous ammonia passed in during 45 mins. By cooling in ice the temperature of the solution was held at 5°-10°C. Solution remained clear and colourless. The tube was then stoppered and allowed to stand at room temperature for $1\frac{3}{4}$ hrs. This solution was then diluted with alcohol and made up to 100 ml. Aliquot portions were subjected to test:

(a) 5 ml. portions of the ammoniacal solution were analysed for guanidine in the usual way. To avoid continued amination in aqueous solution the guanidine picrate precipitate was filtered off after only 30 mins. standing.

Total guanidine = 1.745 g.
Amination at this stage = 74.1 per cent of possible.

The filtrate from these determinations was allowed to stand overnight and the additional guanidine picrate which separated collected, dried and weighed.

Found: Total guanidine = 0.204 g.
Amination = 8.7 per cent of maximum

.'. Total extent of amination = 82.8 per cent of maximum.

(b) 20 ml. of the ammonical solution above was heated 2 hrs. at 60°C. in a stoppered flask. Resulting solution was cooled, diluted with water and made up to 50 ml. 10 ml. portions of the solution were analysed for guanidine in the usual way.

Found: Total guanidine = 2.292 g.
Amination = 97.3 per cent of maximum

(c) 50 ml. of the ammoniacal solution was evaporated to dryness and residue dried to constant weight at 100°C.

Weight of residue	5.170 g.
Weight of corresponding ethylation mixture	5.595 g.
Loss of weight	0.425 g.

Product was analysed for guanidine.

Found: Total guanidine 0.983 g.
Maximum amination requires 1.178 g.
Amination = 83.5 per cent of maximum

(ii) Quantitative Experiments

A series of experiments were carried out to determine optimum conditions of time and ammonia concentration for conversion of ethyl isourea to guanidine.

Alcoholic Ammonia Solution

A solution of ammonia in absolute alcohol was prepared and analysed.

Solution contained 70.76 g. NH_3/litre.

O-Ethyl Isourea

60 g. urea (1 mol.) and 154.0 g. (1 mol.) ethyl sulphate were reacted at 110°C. for 30 mins. Product was analysed as usual for acidity and guanidine after aqueous amination.

Found: Acidity, as $EtHSO_4$, 12.47 g. = 9.89 per cent on D.E.S.
Guanidine, 42.52 g. = 72.06 per cent on urea

Method

Portions of the molten ethylation mixture (7-8 g.) were poured into a weighed stoppered conical flask and weighed. To the viscous fluid was added the requisite volume of alcoholic ammonia, the flask stoppered, shaken to produce a uniform solution and heated in a thermostat at 60°C. for the requisite period of time.

The final solution was cooled, diluted with water and made up to 100 ml. Portions, 5 ml., of the solution were analysed for guanidine in the usual way. Ammonia concentrations of 0.8, 0.9, and 1.0 moles per mole urea were used, in each case additional ammonia equivalent to the acidity of the material being added. Times of reaction were between ½ hr. and 3 hrs.

Data from these experiments are given in Table V.

Table V

Temp. of amination, 60°C.

Moles NH_3 Per Mole Urea	Amination as % of possible maximum				
	½ hr.	¾ hr.	1 hr.	2 hr.	3 hr.
0.8	64.8	63.3	64.9	67.2	73.0
0.9	65.0	65.5	70.8	70.7	82.5
1.0	62.4	62.8	62.6	77.5	77.0

Note: The values, showing extent of amination, obtained by this method were not considered satisfactory; the method was therefore abandoned.

B. Amination of reaction mixture alone using gaseous ammonia

Since alcohol is formed by the amination of O-ethyl-isourea it did not appear necessary to dissolve the original reaction mixture in alcohol prior to examination as described under A. Furthermore, concentration effects would be more marked, and possibly more favourable using the original reaction mixture. Experiments were therefore carried out to test the ideas.

(i) Quantities used: Urea, 6.0 g. (1.2 mol.)
Diethyl sulphate, 12.83 g. (1.0 mol.)

Ethylation of urea, using the above quantities, was effected at 110°C. for 30 mins. When ethylation was complete the mixture was cooled to 60°C. and then gaseous ammonia was bubbled in with good stirring. Initially it was necessary to apply heat to the mixture to maintain the temperature but after 3-5 mins. a slightly exothermic reaction set in and slight cooling was necessary to maintain the temperature at 60°C. As passage of ammonia continued the liquid became progressively less viscous. After 35 mins. evolution of heat ceased and heat was applied to maintain the temperature while ammonia was passed in for a further 55 mins.

The product was a clear colourless liquid which crystallised below 55°C. to a white sticky mass.

Weight of product 19.35 g.

Increase in weight after amination, 0.52 g.

The product was dissolved in water, in which it was readily soluble with considerable absorption of heat, giving a clear colourless solution. The solution was made up to 200 ml. and 5 ml. portions analysed for guanidine.

Found: Total guanidine = 3.955 g.

≡ 80.42 per cent on diethyl sulphate.

In view of the success of this experiment two larger scale experiments were carried out to obtain further information.

(ii) Quantities used:

Urea	72.0 g.	(1.2 mol.)
Diethyl Sulphate	154.0 g.	(1.0 mol.)

Using the above quantities ethylation was carried out at 110°C. for 30 mins. The reaction was performed in a three neck flask fitted with stirrer and thermometer.

When ethylation was complete the flask was fitted with a gas inlet tube dipping below the liquid level and an outlet tube connected to a trap cooled at -25° to -30°C.

The ethylation mixture was cooled to 60°C. and a stream of ammonia passed in with good stirring. Ammonia leaving the flask was passed through the cold trap to condense any alcohol entrained with it.

The somewhat exothermic reaction was again observed as in (i) and the reaction mixture gradually became noticeably less viscous. Evolution of heat ceased after about 1 hour and heating was applied to maintain the temperature at 60°C. for a further 45 mins. ammonia being passed in the whole time.

The stream of ammonia was shut off and the cold trap examined. It was found to contain a quantity of alcoholic ammonia plus a little white solid.

Total weight, 12.4 g.

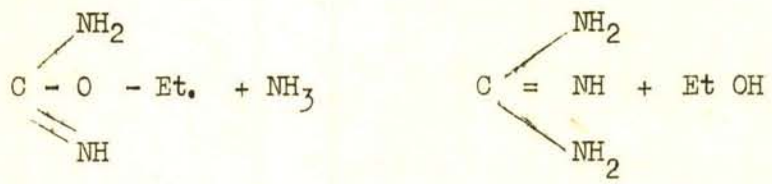
A fresh cold trap was connected to the apparatus and the flask slowly evacuated on the water pump, the temperature of the reaction mixture being raised to 105°C. After 1 hr. at 105°C. the trap was again examined and found to contain alcohol free from ammonia.

Weight, 11.7 g.

The reaction product was finally freed from volatile matter by heating 1 hour at 100°C./1 mm.

Weight of reaction product	201.2 g.
Nett loss in weight, after amination	24.8 g.

In the reaction



88 59

a loss in weight of 29 grms = formation of 59 grms. guanidine from 88 grms. ethyl isourea.

Therefore loss of 24.8 g = formation of 50.5 g. guanidine.

The reaction mixture on cooling was a soft, sticky solid. This solid was analysed for guanidine.

Found: Total guanidine 46.38 g.

$\equiv$ 78.61 per cent on diethyl sulphate.

The bulk of product, referred to as guanidine ethyl sulphate (BI)., was set aside for further experiments on hydrolysis (see below).

(iii) Quantities used:

Urea, 72.0 g (1.2 mol.)
Diethyl sulphate, 154.0 g (1.0 mol.)

Experiment was repeated, greater care being used to collect all alcohol formed in the reaction. Ammonia was passed into the mixture at 60°C. at such a rate that as far as possible all ammonia was absorbed. The outlet from the flask led throughtwo cold traps in series.

Total period of amination was 1 hr. 50 mins. The reaction mixture was allowed to stand overnight when some solid separated in fine plates.

The apparatus was pumped out on the water pump, temperature of the material being raised slowly to 100°C. The material was finally held at 100°C./60 mm. for 1 hr. and the contents of the cold traps examined. Distillate was found to consist of alcohol with a little ammonia and a small quantity of white solid which on preliminary examination appeared to be ammonia carbonate.

Wt. of alcohol, 36.7 g.

= formation of 47.08 g. guanidine.

This residue from the distillation was further heated $1\frac{1}{2}$ hours at 100°C./1 mm. then cooled, weighed and analysed for guanidine.

Weight of reaction product 201.9 g.

Nett loss in weight after amination, 24.1 g.

$\equiv$ formation of 49.04 g. guanidine.

The reaction product was analysed.

Found: Total guanidine, 46.47 g.

$\equiv$ 78.75 per cent on diethyl sulphate.

The bulk of product referred to as guanidine ethyl sulphate BII, was set aside for hydrolysis experiments. (See below).

24. Action of heat on Guanidinium ethyl sulphate

The possibility of converting guanidinium ethyl sulphate to guanidine sulphate and diethyl sulphate was examined. Previous work had shown that excellent yields of diethyl sulphate could be obtained either by heating sodium ethyl sulphate in vacuum (4), or by heating a mixture of ethyl hydrogen sulphate and sodium sulphate invacuum (5).

Note:

$$Gu \equiv \left[C \begin{matrix} \diagup NH_2 \\ - NH_2 \\ \diagdown NH_2 \end{matrix} \right]^{+}$$

(i) Action of heat on Gu Et SO_4 at atmospheric pressure

A small quantity (2.060g.) of guandinium ethyl sulphate (Material from batch B II, previous section) was placed in a boiling tube fitted with a thermometer and an exit tube connected to a nitrometer for the collection of gaseous products. The whole was heated in a bath of butyl phthalate. The following observations were made:

A clear melt was obtained at 115°C.; the temperature was raised slowly to 140°C.; time of heating 15 mins.

At 140°C very slight evolution of gas observed. Continued heating to 165°C.; time of heating, 10 mins.

At 165°C. temperature held steady for 10 mins. No increase in the rate of gas evolution observed. Continued heating to 185°C.; time of heating, 30 mins.

At 185°C. Gas evolution still extremely slow. Material allowed to cool.

Material was remelted 2 hours later; a clear melt was not obtained but it was not possible to decide whether turbidity was due to the presence of gas or solid. Melt was heated at 210°C for 1 hr. Some sublimate was observed in the gas delivery tube and a little oily liquid in the cooled parts of the apparatus (diethyl sulphate?). Gas evolution was still slow. All gas evolved dissolved readily in aqueous sodium hydroxide; gas apparently was not ethylene.

Material remaining in the apparatus solidified on cooling to a pale yellow glass which dissolved readily in water to give a clear, somewhat acid solution.

Solution was made up to 50 ml. and 10 ml. portions analysed for guanidine.

Found:	Total guanidine	0.315g.
	Original guanidine	0.474g.
	Loss of guanidine	33.6 per cent

(ii) Action of heat on Gu. Et. SO_4 in vacuum

Quantity used: Guanidine Ethyl Sulphate (Materialsfrom batch B II),26.03g.

The above material was heated in a vacuum distillation apparatus at 1-3 mm. Hg. Over a period of 80 mins. the temperature was raised from 120-225°C. In the early stages some well crystallised material sublimed into the condenser. There was some evolution of gas at first, later the melt appeared to be boiling but no distillate was obtained. On continued heating solid accumulated gradually in the colder parts of the apparatus and a trace of oily liquid was observed in the condenser.

The temperature of the mass was raised and maintained at 260°-280°C/ 1-3 mm. for 1 hour. Again there appeared to be vigorous boiling but no distillate was collected. Under these conditions the material discoloured badly and heating was discontinued.

Residue was a dark brown, viscous material readily soluble in water.

Weight of residue	16.41g.
Loss of weight on heating	9.62g.

At the end of experiment a small quantity of an ammoniacal liquor was observed in the cold trap of the vacuum pump.

Expberiment was discontinued.

25. The Hydrolysis of Guanidinium Ethyl Sulphate

(i) Preliminary Experiment

Quantities used:	Guanidine Ethyl Sulphate (B II)	25.28g.
	N/I Sulphuric Acid	5.0 ml.

The above quantities were mixed and boiled together under reflux. B.P. of liquid was 130°C.

After 45 mins. it was found that the liquid was alkaline and ammoniacal. An attempt to distil the ammonia into N/I sulphuric acid was unsuccessful; only a trace was obtained.

After a total period of $2\frac{1}{4}$ hours boiling a further 1 ml. of N/I Sulphuric acid was added and liquid boiled for $1\frac{1}{4}$ hours. At the end of the period solution was again found to be ammoniacal but boiling was continued for a further 30 mins. Sulphuric acid,3 ml. N/1,was again added and boiling continued for 1 hr.; solution again showed alkalinity.

It was decided to make the medium strongly acid and 1.814g. concentrated sulphuric acid was added. After 1 hr. boiling the B.P. of the liquid fell to 105°C and the formation of alcohol was detected.

A quantity of liquid was carefully distilled off causing B.P. to rise from 105°-119°C. (25 minutes). This material was found to be aqueous alcohol.

Weight of aqueous alcohol 3.03g.

Density at 20°C.,0.837g./cc. ≡ 82.6 per cent Ethyl alcohol

Weight of alcohol recovered, 2.50g.

Hydrolysis of all guanidine ethyl sulphate requires formation of 4.54g. alcohol.

The remaining liquid was allowed to boil under reflux for a further period of 45 mins. No further fall in boiling point occurred although the liquid possessed an odour of alcohol. The liquid was cooled when crystallisation commenced at 75°C. The material was dissolved in water and made up to 250 ml.

Solution was analysed for acidity and guanidine.

Found:	Total guanidine	5.57g.
	Origianl "	5.82g.
	Loss of Guanidine	4.3 per cent
	Total acid, as H_2SO_4	5.240g.
	H_2SO_4 added	2.204g.
	Free H_2SO_4 formed on hydrolysis	3.036g.
	Hydrolysis of guanidine ethyl sulphate requires formation of	4.833g. H_2SO_4
	Loss of H_2SO_4 =	1.797g.

(ii) Quantitative Experiments

On the basis of the foregoing experiment a series of quantitative experiments was carried out to determine optimum conditions for complete hydrolysis of guanidinium ethyl sulphate, maximum recovery of ethyl alcohol and minimum loss of guanidine.

General Method

About 25g. of guanidinium ethyl sulphate was mixed with the requisite quantities of water and concentrated sulphuric acid (97.9 per cent) and the whole boiled under reflux till hydrolysis appeared complete. This was indicated by the attainment of a steady minimum for the boiling point of the liquid.

The liquid was then carefully fractionated at normal pressure, distillate being accepted until the boiling point of the liquid reached 120-125°C. The distillate was weighed and the alcohol content estimated by determination of its density.

All remaining alcohol and water was then distilled under diminished pressure and finally at 20-30 mm., bath temperature 100°C., the distillate being collected in a trap immersed in a cooling bath of drikold/trichlorethylene. The weight and alcohol content of this distillate was also determined. Total alcohol recovery was expressed as % of ethyl group present in original diethyl sulphate.

The residue was dissolved in water, made up to 250 ml. and analysed for total acidity and guanidine. The loss, or fixation, of sulphuric acid and loss of guanidine could then be calculated.

The experimental conditions together with analytical data and material balances are given in Table VI.

TABLE VI

Reaction Mixture	I	II	III	IV	V	VI	VII
Gu. Et SO_4 BI g.		25.25				25.20	25.28
Gu. Et SO_4 BII g.	25.39	-	25.23	25.15	25.18	-	-
H_2SO_4 (100%) g.	0.80	1.01	1.54	2.01	2.48	2.95	3.43
Total water g.	7.02	7.02	7.04	7.05	7.09	7.04	7.07
Hydrolysis							
Time of hydrolysis, mins.	90	90	90	30	15	10	5
Initial B.P. °C.	115	112	119	110	114	115	117
Final B.P. °C.	105	94	100	94	99	98	98
Alcohol Distillate: 1st. fraction							
Weight recovered (100%) g.		2.75	3.79	3.80	3.75	3.62	3.76
Concentration %	-	81.8	84.5	82.5	80.3	84.2	82.2
% of Total recovered	-	60.2	73.8	68.8	68.9	66.9	68.3
Alcohol Distillate: 2nd. fraction							
Weight recovered (100%) g.		1.82	1.34	1.73	1.69	1.79	1.75
Concentration %	-	28.1	27.3	31.8	32.7	32.8	33.6
% of Total recovered	-	39.8	26.2	31.2	31.1	33.1	31.7
Total recovery of alcohol							
Weight recovered (100%) g.	1.58	4.57	5.13	5.53	5.44	5.41	5.51
As % on Diethyl Sulphate	13.7	39.6	44.6	48.2	47.4	47.0	47.7
Water Balance							
Recovered in 1st Et OH distillate g.	-	0.61	0.69	0.81	0.92	0.68	0.82
" " 2nd " " g.	-	4.66	3.56	3.71	3.48	3.66	3.46
Total H_2O recovered g.	4.17	5.27	4.25	4.52	4.40	4.34	4.28
Used in hydrolysis g.	7.02	7.02	7.04	7.05	7.09	7.04	7.07
Consumed in hydrolysis g.	0.62	1.79	2.01	2.16	2.13	2.12	2.16
In final Gu HSO_4 residue g.	2.23	0.00	0.78	0.37	0.56	0.58	0.63
Guanidine Balance							
Before hydrolysis g.	5.84	5.82	5.81	5.79	5.80	5.81	5.83
After hydrolysis g.	5.70	5.93	5.66	5.66	5.70	5.88	5.78
Difference %	-2.40	+1.89	-2.58	-2.25	-1.72	+1.21	-0.86
H_2SO_4 Balance							
Total, free, in Gu HSO_4 residue (a) g.	0.00	4.09	6.02	7.11	7.74	8.33	8.79
Equivalent to Et OH recovered (b) g.	1.68	4.87	5.46	5.89	5.79	5.76	5.87
Used in hydrolysis (c) g.	0.80	1.01	1.54	2.01	2.48	2.95	3.43
Loss, or fixed as salt, b + c - a, g.	2.48	1.79	0.98	0.79	0.53	0.38	0.58
Loss, % on Total (b + c).	100	30.45	14.00	10.00	6.41	4.36	6.24

(iii) Large scale experiment

Using quantities parallel to those used in Experiment V, Table VI, a large scale experiment was carried out to obtain some guanidinium hydrogen sulphate suitable for nitration studies.

Quantities used:

Guanidinium ethyl sulphate, material BI,	106.0g.
Water	29.7g.
H_2SO_4 (10.7g. of 97.88% H_2SO_4), 100%	10.5g.

The above quantities were mixed and boiled under reflux, the changes in boiling point of the liquid, thermometer in liquid, with time being observed. Valves observed were:-

Time of boiling, mins.	0	1.5	3	4.5	7.5	11	14.5	20
B.P. °C.	115	114	111.5	109	108	106	104	104

After refluxing for 20 mins. the flask was fitted with a vigreux column and the alcohol fractionally distilled whilst the temperature of the boiling liquid rose to 120°C.; the distillation, i.e. at atmospheric pressure, was stopped at this stage.

Alcohol Distillate 1st. Fraction

Total weight of aqueous alcohol distillate,	14.3g.
Density of distillate, at 20°C.	0.8464g./c.c
Concentration of alcohol	78.8 per cent
Weight of alcohol (100%) in distillate	11.3g.
Weight of water in distillate	3.0g.

The residual liquid was now distilled under diminished pressure to remove remaining alcohol and water, and finally heated at 100°C. at 20 mm. for 30 mins. This second distillate was combined with the first fraction and the overall alcohol concentration determined by density method.

Alcohol Distillate, 2nd. Fraction

Total weight of aqueous alcohol distillate,	25.2g.
Concentration of alcohol	36.9 per cent
Weight of alcohol (100%) in distillate	9.3g.
Weight of water in distillate	15.9g.

Alcohol Balance

Alcohol recovered, total 20.6g.

= 42.4 per cent on diethyl sulphate

Water Balance

Water recovered, total	18.9g.
Water used in hydrolysis	29.7g.
Water consumed in hydrolysis (= Et. OH formed)	8.1g.
Water remaining in residue after distillation	2.7g.

Distillation residue

The residue was viscous liquid which could be induced to crystallise but remained as a supercooled liquid. It was analysed for guanidine and total acidity.

Weight of residue, 105.9g. (cf. 106.9g. theory)

Found: Total guanidine before hydrolysis, 24.44g.

Total guanidine after hydrolysis, 24.50g.

H_2SO_4 Balance

Total free H_2SO_4 in Gu. HSO_4 residue, a,	31.4g.
H_2SO_4 equivalent to Et.OH liberated, b,	22.0g.
H_2SO_4 used in hydrolysis, c.	10.5g.
Loss of H_2SO_4, i.e. fixed as salt, b + c - a	1.1g.
% loss of H_2SO_4 on total (b + c)	3.39 per cent.

The material from this experiment, known as guanidinium hydrogen sulphate, Batch I, was set aside for nitration studies.

26. Preparation of Guanidinium Hydrogen Sulphate

Further quantities of guanidinium hydrogen sulphate (Gu.HSO_4) were prepared for use in further nitration studies. Preparations were carried out starting from urea in order to make further observations on the various stages of the preparation.

All stages in the preparation of Gu.HSO_4 were carried out in a 3-neck flask fitted with stirrer, gas inlet, thermometer and reflux condenser.

Preparation I

Batch I of Gu.HSO_4 was referred to in previous section.

Preparation II

(a) Ethylation

Diethyl sulphate	308.0 g. (1 mol.)
Urea	144.0 g. (1.2 mol.)

Ethylation was carried out in the usual way at 110°C. A clear solution was obtained in 3 minutes; at the point where the mixture began to clear the reaction was quite exothermic and external cooling was necessary to maintain the temperature. Total period of ethylation was 30 minutes.

The product was a syrupy liquid which was cooled at 60°C. and aminated immediately.

(b) Amination The reaction mixture was well stirred and a stream of gaseous ammonia passed in. As ammonia was absorbed the mixture became rapidly less viscous, there was some evolution of heat and slight cooling was needed to maintain reaction temperature at 60°C.

Excess ammonia was passed out through a trap cooled in ice to condense any entrained ancohol.

Total time of amination was $2\frac{1}{2}$ hours, by whichtime evolution of heat had almost ceased. The mixture was allowed to stand overnight and on cooling deposited some crystalline material.

The flask was next connected to a vacuum pump and excess ammonia drawn off without heating. The cold trap was cooled in a Drikold/trichlorethylene mixture to condense all alcohol. When evolution of ammonia ceased the flask was gradually heated in a water bath to remove alcohol. Removal of volatile matter was completed by heating for 1 hour at 100^{o}C./25 mm. Hg.

The alcohol distillate thus obtained contained a little white solid and some dissolved ammonia. The ammonia content was estimated and the weight of pure alcohol obtained.

Alcohol recovered, weight 73.5 g. $\equiv$ 39.97 per cent. on diethyl sulphate

Residue, weight 404.9 g.

(c) Hydrolysis

To the residue from the amination stage was added:

Water	80.5 g.
H_2SO_4 (97.59 per cent).	42.6g.

and the whole boiled under reflux for 20 minutes. After 13 minutes the boiling point of the liquid fell from 114^{o} - 104^{o}C. when it remained steady for the rest of reflux period.

Alcohol and water were distilled off from the mixture initially at normal pressure using the reflux condenser, drained of water, as a fractionating column. Distillation was completed in vacuo and material finally heated 1 hour at 100^{o}C./25 mm.

Residue was allowed to cool overnight and was then found to be a somewhat viscous liquid which could be induced to crystallise to a solid, Freezing Point 52^{o}C.

Material was analysed for guanidine and total acidity.

Residue

Weight of residue	405.9 g.
Total acidity, as H_2SO_4	118.4 g.

H_2SO_4, fixed as salt during hydrolysis, 2.56 g. $\equiv$ 2.16 per cent. on total (H_2SO_4 equivalent to Et.OH liberated + H_2SO_4 added for hydrolysis).

Total guanidine, weight 9.21 g. $\equiv$ 22.69 per cne.t on residue

$\equiv$ 78.05 per cent .on diethyl sulphate

Alcohol distillate

Alcohol distillate, weight	121.0 g.
Alcohol content	61.6 per cent.
Alcohol recovered, weight	74.51 g.

≡ 40.52 per cent. on diethyl sulphate

This material, referred to as Gu.HSO_4 II, was set aside for nitration.

Preparation III

Owing to the efficient recovery of alcohol and sulphuric acid from the hydrolysis stage it was decided to revert to a molar ratio of urea: diethyl sulphate 1:1, and thus avoid to some extent the presence of nitrogenous impurities at the nitration stage.

(a) Ethylation

Diethyl sulphate	308.0 g. (1 mol.)
Urea	120.0 g. (1 mol.)

Ethylation carried out the usual way at 100°C. Mixture became clear after 9 minutes. Reaction at this stage was somewhat exothermic but temperature readily controlled. After 16 minutes all evolution of heat had ceased. Total period of ethylation was 60 minutes.

(b) Amination

Material from ethylation was cooled to 60°C. and aminated as in the previous experiment. Passage of ammonia was much faster and more efficient cooling was needed to maintain the temperature at 60°C. A marked smell of ether was observed in the exit gas from the apparatus.

Evolution of heat ceased after passing ammonia for 1 hour. Passage of ammonia was continued for a further 15 minutes and the material allowed to stand overnight. On cooling it was found that separation of crystalline matter commenced at 35°C.

Distillation of alcohol was carried out as previously described.

Residual material, weight	384. 10 g.
Alcohol recovered, weight = 70.71 g. ≡	38.43 per cent. on diethyl sulphate

(c) Hydrolysis

To the residue from amination stage was added:

Water	76.48 g.
H_2SO_4 (97.57 per cent.)	36.04 g.

The whole was boiled under reflux for 30 minutes. The boiling point of the clear solution fell during this period from 118°C. to 104°C. Distillation of the liberated alcohol was carried out as previously described. The distillate and residue were analysed.

Residue

Weight of residue 376.58 g.

Total guanidine, weight 85.06 g. ≡ 22.58 per cent on residue
≡ 72.07 per cent. theory, on urea

Total acidity, as H_2SO_4 114.1 g.

H_2SO_4, fixed as salt during hydrolysis, 1.6 g.
≡ 1.38 per cent on total (H_2SO_4 equivalent is Et.OH liberated + H_2SO_4 added for hydrolysis).

Water content of residue (Karl Fischer value), 0.96 per cent.

Alcohol distillate

Weight of alcohol distillate 119.17 g.

Concentration of alcohol in distillate 63.4 per cent.

Weight of alcohol (100 per cent.) recovered, 75.58 g.
≡ 41.08 per cent. on diethyl sulphate

Treatment of residue The residue was found to have a freezing point of 63°C. In order to avoid crystallisation it was diluted with concentrated sulphuric acid whilst still warm in the proportions:

Residue 362.8 g.

H_2SO_4 (97.57 per cent). 151.4 g.

An appreciable evolution of heat occurs when the residue is mixed with concentrated sulphuric acid. The solution was used for nitration studies (see below).

Preparation IV

Material was prepared similarly to Gu.HSO_4 III using double quantities

(a) Ethylation Identical

(b) Amination Total period of amination 2½ hours.

Material product commenced to crystallise at 47°C., i.e. before distillating off alcohol.

Alcohol recovered 150.1 g.
≡ 40.8 per cent. on diethyl sulphate

Weight of residue after distillation of alcohol = 772.1 g.

Melting point of residue, 93°C.

(c) Hydrolysis A more prolonged hydrolysis was carried out in order to obtain a material with better nitration characteristics.

Sulphuric acid (97.57 per cent.) 78.6g.

Water 153.5g.

(i) The above quantities of water and sulphuric acid were added to the residue from the amination stage and the whole boiled, under reflux for 30 minutes. Boiling point of the liquid fell from 112°C. to 104°C.

(ii) Alcohol distilled off at normal pressure in 15 minutes; boiling point rose 104°C. to 115°C.

(iii) Material again refluxed 15 minutes; boiling point fell from 115°C. to 110°C.

(iv) Alcohol distilled off in 5 minutes; boiling point rose 110°C. to 115°C.

(v) Material again refluxed 15 minutes; boiling point fell from 115°C. to 114°C.

Remaining alcohol and water were distilled off in the usual way under diminished pressure. The residue and distillate were analysed.

Residue

Weight of residue	757.1 g.
Freezing point	64°C.
Total guanidine, weight	171.9 g. $\equiv$ 22.70 per cent. on residue.
	$\equiv$ 72.81 per cent. theory, on urea.

Total acidity, as H_2SO_4, 33.13 per cent, = 235.7 g.

H_2SO_4, fixed as salt during hydrolysis, 11.1 g.

$\equiv$ 4.50 per cent. on total (H_2SO_4 equivalent to Et.OH liberated + H_2SO_4 added for hydrolysis).

Alcohol distillate

Weight of alcohol distillate,	244.1 g.
Concentration of alcohol in distillate	65.4 per cent.
Weight of alcohol (100 per cent.) recovered,	159.7 g.
	$\equiv$ 43.41 per cent. on diethyl sulphate

Preparation V

To investigate stability of o-ethyl isourea and guanidine during preparation of guanidine hydrogen sulphate

1. A preparation of gunidine hydrogen sulphate was carried out starting from urea and diethyl sulphate. At every stage a sample was taken and analysed for guanidine or o-ethyl isourea via guanidine to determine what loss of yield occurred during the various operations.

Ethylation

Diethyl sulphate	231.0 g. (1 mol.)
Urea	90.0 g. (1 mol.)
Temperature of ethylation	110°C.
Time for reaction mixture to clear	4 mins.

Ethylation (contd.)

Total period of ethylation	30 mins.
Ethylation mixture, weight	320.1 g.
Loss in weight on ethylation	0.9 g.

Sample of material after aqueous amination gave, on analysis:

Total guanidine = 60.75 g. ≡ 68.64 per cent. on urea

Amination

Ethylation mixture, weight used	311.2 g.
Amination time, using NH_3 gas	1 hr. 40 mins.
Amination temperature	70-79°C.
Amination mixture, weight	332.6 g.
Ammonia absorbed, weight	21.4g.

By Analysis:

Total guanidine = 63.92 g. ≡ 72.21 per cent. on urea

Alcohol distillation

Amination mixture, weight used	265.1 g.
Residue from distillation	223.7 g.

Total loss in weight ≡ 53.4 g. (corrected to original weight, 320.1 g., of ethylation product)

Total ammonia absorbed at amination stage = 22.0 g. (corrected)

Therefore effective loss in weight = 31.4 g. (corrected)

Formation of 1 mole guanidine ≡ 29 g. loss in weight

Total guanidine formed = 63.89 g. (theory)
≡ 72.18 per cent. on urea.

Hydrolysis

Distillation residue, weight used	165.5 g.
Residue + H_2SO_4/H_2O	216.5 g.
Hydrolysis time	30 mins.

By analysis:

Total guanidine = 64.34 g. ≡ 72.69 per cent. on urea.

Alcohol distillation

Hydrolysis mixture	151.6 g.
Distillation residue	115.5g.

By analysis:

Total guanidine = 64.42 g. ≡ 72.78 per cent. on urea.

Collected data are shewn below:

Stage	% yield of guanidine on urea
Ethylation (aqueous amination)	68.64
Amination (gaseous ammonia)	72.21
Alcohol distillation, 1st (theoretically)	72.18
After hydrolysis	72.69
Alcohol distillation, 2nd	72.78

27. Nitration of Guanidinium Hydrogen Sulphate

Note. By guanidinium hydrogen sulphate, Gu. HSO_4, is meant the product of hydrolysis which has been almost totally freed of alcohol and water by distillation. The product contains a high percentage of guanidine, ca. 72 per cent. based on urea, as guanidinium salt and impurities, the exact nature of which are as yet to be investigated.

The nitration of Gu.HSO_4, batches of which were prepared as described in previous section, was studied in order to examine its behaviour and define the conditions for maximum conversion to nitroguanidine (picrite).

Note. The order of study of the various parameters, indicated in this section, is to be regarded as arbitrary. The choice of succesive parameters was determined usually by earlier results. The work was conducted in this manner in order to achieve a more rapid assessment of the nitration stage.

A. Effect of varying the molar ratio Gu. H_2SO_4: HNO_3, keeping all other parameters constant, on the yield of nitroguanidine.

Preliminary experiments
General Method

A quantity of the guanidinium hydrogen sulphate material was run into a beaker and the requisite quantity of concentrated sulphuric acid added with stirring. At this stage a considerable evolution of heat occurred. It was established by experiment that this evolution of heat could not be attributed to the water present in the material. If excessive cooling was applied at this stage the material tended to solidify and did not then dissolve readily in the sulphuric acid.

The sulphuric acid solution was cooled to 10°C and the requisite quantity of 98% nitric acid added slowly with good stirring the temperature being maintained below 25°C by external cooling. When addition of nitric acid was complete the mixture was allowed to stand for 3 hours, the temperature being held below 30°C by cooling as necessary. At this stage considerable evolution of gas occurred (CO_2 and N_2?); there was also appreciable evolution of heat.

When the period of standing had elapsed the material was drowned on to a sufficient quantity of ice and water to dilute the sulphuric acid to 20 per cent concentration. The precipitated nitro guanidine was filtered, well washed with water, retransferred to a beaker, triturated with water (100 ml.). and again filtered and washed; it was dried to constant weight overnight at 100°C.

The experimental data are given in Table VII.

Table VII

Temperature of nitration, 25 - 30°C.

NITRATION	I	II	III	IV	V
GU. H.SO4. (Batch I) g.	20.4	19.7	19.4	20.7	19.1
Guanidine (GU) g.	4.7	4.6	4.5	4.9	4.4
Sulphuric Acid					
Added (97.6%) g.	10.1	9.8	13.5	14.5	17.3
Total present g.	16.1	15.6	19.3	20.6	22.9
Moles. per. mole GU.	2.06	2.04	2.58	2.53	3.13

Table VII (Contd.)

NITRATION	I	II	III	IV	V
Nitric Acid					
Added g.	5.3	6.4	5.0	6.7	6.2
Moles for Mole GU.	1.06	1.30	1.04	1.28	1.14
Nitroguanidine					
Yield g.	5.1	5.2	4.6	6.0	4.9
Yield on GU. %	61.6	64.1	58.0	69.5	63.2

Additional Observations

I. Temperature of nitration mixture on standing did not exceed 28°C.

II. Temperature of nitration mixture on standing did not exceed 29°C.

On addition of sulphuric acid prior to nitration a little solid was deposited. This redissolved on addition of nitric acid.

III. Temperature of nitration mixture on standing did not exceed 30°C. Solution was cooled strongly on addition of sulphuric acid; a considerable quantity of hard white solid separated and did not redissolve. Material dissolved slowly on standing after addition of nitric acid. Nitration mixture was very yellow.

IV. Addition of sulphuric acid caused temperature of mixture to rise to 55°C. No solid separated on cooling. During standing of nitration mixture temperature once reached 38°C. otherwise 30°C. was not exceeded.

V. Addition of sulphuric acid caused temperature of mixture to rise to 52°C. No solid separated on cooling. During standing of nitration mixture temperature once reached 42°C. otherwise 30°C. was not exceeded.

B. The stability to heat of a solution of Guanidinium hydrogen sulphate, $Gu.HSO_4$, in concentrated sulphuric acid.

In view of the heat evolution which occurred when sulphuric acid was added to guanidine hydrogen sulphate an experiment was carried out to determine whether any degradation of guanidine took place when the materials were heated together.

A mixture of $Gu.HSO_4$ (Batch II) and concentrated sulphuric acid with the ratio of 2.11 moles sulphuric acid per mole guanidine was used for these experiments. This mixture was heated successively at 60°, 80° and 100°C, changes in guanidine content and total acidity being observed at each stage.

Details of experiment together with analytical data are given below.

Reaction Mixture

Guanidine hydrogen sulphate, (Batch II), used	25.82g.
Sulphuric acid 97.59%, used	13.31g.

Molar ratio, Guanidine: H_2SO_4, 1.00: 2.11

Total acidity, as H_2SO_4 (calculated)	52.44 per cent
Guanidine content (calculated)	14.97 per cent.

(a) Heating at 60°C

Time of heating	90 mins
Weight of initial mixture	39.13 g.
Loss of weight on heating	NIL
Total acidity after heating (H_2SO_4)	52.14 per cent
Loss of sulphuric acid	0.58 per cent
Guanidine content after heating	15.00 per cent
Loss of guanidine	NIL

At this stage there was no apparent degradation

(b) Heating at 80°C.

Time of heating	90 mins.
Weight of mixture from (a)	34.18 g.
Loss of weight on heating	0.01 g.
Total acidity after heating (H_2SO_4)	51.98 per cent.
Loss of sulphuric acid.	0.31 per cent.
Guanidine content after heating	15.00 per cent.
Loss of guanidine	NIL

At this stage there was a very slow evolution of gas.

(c) Heating at 100°C

Time of heating	75 mins.
Weight of mixture from (b)	27.45 g.
Loss of weight on heating	0.07 g.
Total acidity after heating (H_2SO_4)	51.87 per cent.
Loss of sulphuric acid	0.21 per cent.
Guanidine content after heating	14.92 per cent.
Loss of guanidine	0.53 per cent.

During this stage evolution of gas was more rapid than at 80°C but still very slow.

Residue from this experiment was nitrated to examine ease of nitration and yield of nitroguanidine.

Nitration of Residue

To study effect of nitration at 20°C. using the molar ratio, Gu:H_2SO_4: HNO_3, 1.0: 2.04: 1.30 (cf. Exp. II Table VII) on the yield of nitroguanidine.

Material used	21.85 g.
Nitric Acid (98 per cent) used,	4.68 g.

Molar ratio H_2SO_4: HNO_3: Guanidine, 2.11:1.35: 1.0

Time of addition of HNO_3	10 mins.
Temperature of nitration	6 - 9°C.
Time of stirring	10 mins.
Temperature during stirring	9 - 21°C.

Nitration mixture was allowed to stand at 20°C. for a further 50 mins.; only very slight cooling was necessary to hold the temperature of the mixture.

Nitration mixture was drowned on to sufficient ice and water to dilute all sulphuric acid to 20 per cent concentration. Precipitated nitroguanidine was filtered, well washed with water, retransferred to a beaker, triturated with water (100 ml.) and again filtered and washed; dried overnight at 100°C.

Nitro guanidine 3.65 g.

$\equiv$ 63.5 per cent on guanidine.

Nitration og Gu. HSO_4 using the molar ratio. Gu: H_2SO_4 : HNO_3, 1.0 : 2.59 : 1.32.

For purposes of comparison with the foregoing nitration a direct nitration of guanidine hydrogen sulphate was carried out. The molar ratio of reactants differed slightly.

Gu. HSO_4, Batch II	25.36 g.
Sulphuric acid (98 per cent.)	17.68 g.
Nitric acid (98 per cent.)	8.30 g.

Molar ratio, Gu: H_2SO_4 : HNO_3 = 1:2.59:1.32

The guanidine hydrogen sulphate was stirred and sulphuric acid added gradually over a period of 5 mins. Sufficient cooling was applied to keep the temperature below 30°C.

The resulting solution was cooled more strongly and nitric acid added slowly with stirring over a period of 10 mins. Temperature of addition of nitric acid was 5-10°C.

The reaction mixture was stirred for 10 mins. without cooling when the temperature rose to 20°C. and then stirred for 1 hour controlling temperature at 20°C. Evolution of gas and heat was much greater than in the previous nitration. Frothing became serious and only by vigorous stirring could this be controlled.

The reaction mixture was drowned onto ice and water, in the ratio 4 parts per part sulphuric acid. The precipitated nitroguanidine was collected as previously described using water as washing medium and dried overnight at 100°C.

Nitroguanidine, weight 7.56 g.

$\equiv$ 74.6 per cent on guanidine.

C. Effect of varying the molar ratio, Gu: H_2SO_4: HNO_3, and temperature of nitration, keeping all other parameters constant, on the yield of nitroguanidine.

Nitration of Gu HSO_4 after heating with sulphuric acid

The two previous experiments suggested that the material after heating with sulphuric acid gave less frothing and side reactions on nitration than the untreated material.

A series of nitrations was carried out using three ratios, sulphuric acid: guanidine, and two ratios, nitric acid: guanidine.

Guanidine Hydrogen Sulphate/Sulphuric Acid Solutions

Mixtures of Gu.HSO_4, Batch II, and sulphuric acid in the requisite proportions were made up and heated 2 hrs. at 80°C. in stoppered flaks. A check was made on loss in weight which occurred.

(i) Molar Ratio Sulphuric Acid/Guanidine 2.07: 1.00

Guanidine hydrogen sulphate II	112.78 g.
Sulphuric Acid (98 per cent.)	55.98 g.
Loss on heating	NIL

(ii) Molar Ratio, Sulphuric Acid/Guanidine, 2.59: 1.00.

Guanidine Hydrogen Sulphate, II	112.3 g.
Sulphuric Acid (98 per cent)	78.3 g.
Loss on heating	0.1 g.

(iii) Molar Ratio, Sulphuric Acid/Guanidine, 3.11: 1.00

Guanidine Hydrogen Sulphate II	101.4 g.
Sulphuric Acid (98 per cent)	91.2 g.
Loss on heating	0.1 g.

All mixtures became slightly darker in colour on heating and evolved a small quantity of gas.

Nitric Acid Ratios

Two ratios, nitric acid: guanidine were used, 1:1 and 1.25:1 respectively. The high ratio was calculated to give sufficient nitric acid to nitrate all unchanged urea in addition to the guanidine present in the mixture.

General Method

Nitrations were carried out at 0^o and 20^oC. Methods employed were as follows.

Nitration at 0^oC.

Sulphuric acid solution was well stirred and cooled using an ice-salt mixture. Nitric acid was added slowly temperature being held at 0^o to 5^oC. When addition was complete mixture was stirred for a further period of 1 hour at 0^oC and then drowned onto ice and water in the ratio 4 parts ice to 1 part sulphuric acid. Precipitated nitroguanidine was collected as previously described using water as washing medium and dried overnight at 100^oC.

Nitration 20^oC.

Addition of nitric acid was carried out at 5-10^oC. When addition was complete the mixture was allowed to warm up to 20^oC. and then held at this temperature with good stirring for a further 1 hour. Other details were as above.

Data from these nitrations are given in Table VIII.

Table VIII

Time of nitration at 0^oC or 20^oC., 1 hour

Expt.	Mol. Ratio H_2SO_4: Gu.	Mol. Ratio HNO_3: Gu.	Temp of nitration ^oC.	Time in Mins. Addition of HNO_3	To reach 20^oC	Yield of nitroguanidine %	M.P. of * Nitroguanidine ^oC
I	2.07:1.0	1.0: 1.0	0	10	-	17.2	236
II	"	"	20	8	6	48.4	235
III	"	1.25: 1.0	0	13	-	32.9	234
IV	"	"	20	11	6	59.7	236
V	2.59: 1.0	1.0 : 1.0	0	8	-	62.3	235
VI	"	"	20	10	9	67.0	235
VII	"	1.25: 1.0	0	10	-	72.8	237
VIII	"	"	20	11	4	77.0	239
IX	3.11: 1.0	1.0 : 1.0	0	8	-	71.4	238
X	"	"	20	9	8	65.3	236
XI	"	1.25: 1.0	0	11	-	84.0	235
XII	"	"	20	15	7	78.1	236

* With decomposition in all cases.

General Observations

Frothing occurred in all nitrations but at 0°C was much less troublesome than at 20°C. when on occassions very good stirring was needed to break down the froth.

Some nitrations developed a pale green colour which later changed to a creamy yellow. In all cases the mixture had a faint smell of acetaldehyde.

D. Effect of varying molar ratio, Gu:H_2SO_4: HNO_3, and temperature of nitration, keeping all other parameters constant, on the yield on nitroguanidine

A series of nitrations similar to the foregoing, described under (C), was carried out using Gu HSO_4, Batch III.

In this series the Gu.HSO_4 -H_2SO_4 solution was not heated prior to nitration.

Molar ratios Gu: H_2SO_4 : HNO_3 used

Nitric Acid: guanidine ratios used were 1.0: 1.0 and 1.39: 1.0, the latter being sufficient to nitrate all unchanged urea in addition to guanidine present.

Sulphuric acid: guanidine ratios used were 4.15:1, 4.98:1 and 5.81:1.

Nitration temperatures were 0°, 10° and 20°C.

General Method

Sufficient sulphuric acid was added to the guanidine solution to bring up the sulphuric acid/guanidine ratio to the required value.

In nitrations at 0° and 10°C the nitric acid was added at 0° and 10°C respectively the temperature being controlled by external cooling. Addition of nitric acid was followed by a further 1 hr. stirring at the requisite temperature, cooling being applied as necessary.

In nitrations at 20°C. nitric acid was added at 5-10°C, the mixture allowed to warm up to 20°C and then stirred 1 hr. at 20°C.

In all cases the final mixture was drowned into ice and water (4 parts per part sulphuric acid). The drowned mixture was allowed to stand 30 mins. to ensure that all nitro guanidine sulphate had hydrolysed. The nitroguanidine was collected as previously described using water as washing medium and dried overnight at 100°C.

Data from these experiments are given in Table IX.

Table IX

Time of stirring after addtion of HNO_3, 1 hour.

Expt.	Mol. Ratio H_2SO_4: Gu.	Mol. Ratio HNO_3 : Gu.	Temp. of Nitration °C.	Time in Mins. addition of HNO_3	Nitroguanidine Yield %	M.P. °C.*
I	4.15 : 1.0	1.39: 1.0	0	12	82.7	234
II	"	1.0 : 1.0	20	9	64.4	239
III		1.39: 1.0	20	16	80.5	239
IV	4.98: 1.0	1.0 : 1.0	0	8	75.8	235
V	"	1.39: 1.0	0	9	88.5	235
VI	"	1.39: 1.0	10	10	88.5	237
VII	"	1.0: 1.0	20	14	64.6	240
VIII	"	1.39: 1.0	20	17	81.3	239
IX	5.81: 1.0	1.0 : 1.0	20	13	54.4	235
X	"	1.39: 1.0	20	15	70.2	235

* With decomposition

General Observations

Frothing occurred in all nitrations and appeared to be worst at higher temperatures; at 0° and 10° it was easily controlled. In some cases at $20^{\circ}C$ only very good stirring controlled the frothing at all; there seemed a danger that portions of the froth might not be adequately cooled owing to the rather viscous nature of the froth.

In nitrations at $20^{\circ}C$ the development of a greenish and subsequently yellowish colour occurred. This colour was always accompanied by a smell of acetaldehyde. At $0^{\circ}C$. no colours developed and at $10^{\circ}C$. only a very faint tinge.

E. Effect of varying the molar ratio, Gu: HNO_3, and time of nitration keeping all other parameters constant, on the yield of nitroguanidine

A series of nitrations, similar to the foregoing, was carried out using Gu. HSO_4, Batch IV.

Previous nitrations seemed to indicate that for best yields of nitroguanidine a fairly high molar ratio sulphuric acid: guanidine was desirable. To minmise frothing and the development of colour, probably due to degradation of less stable nitramines and oxidation of other impurities, a temperature of nitration not exceeding $10^{\circ}C$ was desirable.

On the basis of these observations a large series of nitrations was carried out to determine optimum conditions of nitric acid/guanidine ratio and time of nitration for maximum yield of nitroguanidine.

Sulphuric Acid Ratio

Sulphuric acid/guanidine ratio used was on the basis of 3 parts H_2SO_4 per part guanidine nitrate, or 3.74 moles. H_2SO_4 per mole guanidine. In calculating the sulphuric acid to be added all sulphuric acid in the material whether free or in combination with guanidine was taken into account. Sulphuric acid used was 98.0 per cent concentration; quantities were calculated to give the requisite quantity of 100 per cent sulphuric acid.

Nitric Acid Ratio

Molar ratios nitric acid: guanidine between 1.0:1.0 and 1.8:1.0 were used. Nitric acid of 98.5 per cent concentration was used; quantities were calculated to give the requisite quantity of 100 per cent nitric acid.

Method of Nitration

The mixture of Gu.HSO_4 and H_2SO_4 was cooled to $10^{\circ}C$ and well stirred. Nitric acid was run in dropwise, temperature being held at $10^{\circ}C$. When addition was complete the mixture was stirred for the requisite reaction period and then drowned onto 250 grams ice and water. The drowned mixture was allowed to stand 30 mins. to ensure complete hydrolysis of nitroguanidine sulphate. The crude nitroguanidine was collected as previously described using initially a saturated, at room temperature, solution of nitroguanidine as washing medium and finally ice water; this procedure was adopted in order to minimise solubility losses. The product was dried overnight, to constant weight, at $100^{\circ}C$.

Experimental conditions together with yield data are given in Table X.

Table X

Temperature of nitration, 10°C.

Molar ratio, Gu: H_2SO_4, 1.0: 3.74 (1 part: 6.21 parts, by weight)

Nitration No.	Mol. Ratio HNO_3:Gu.	Gu. HSO_4 IV Grms.	H_2SO_4 100% g.	HNO_3 100% g.	Time of addition of HNO_3 mins.	Time of stirr-ing mins.	Nitroguanidine		
							Grms.	Guanidine	M.P. °C*
I	1.0 : 1.0	35.22	38.61	8.55	10	60	10.63	75.6	236
II	1.1 : 1.0	36.60	40.15	9.76	13	60	11.66	79.7	236
III	1.2 : 1.0	35.27	38.68	10.25	13	60	11.63	82.4	236
IV	1.2 : 1.0	36.09	39.59	10.73	11	60	12.54	86.9	235
V	1.3 : 1.0	36.58	40.14	11.53	14	30	12.88	88.0	235
VI	1.3 : 1.0	36.27	39.78	11.42	16	60	12.56	86.6	236
VII	1.3 : 1.0	37.51	41.13	11.81	12	90	12.58	83.9	236
VIII	1.4 : 1.0	35.71	39.17	12.10	12	15	13.06	91.4	236
IX	1.4 : 1.0	35.77	39.24	12.14	13	30	12.67	88.5	235
X	1.4 : 1.0	36.25	39.77	12.27	9	45	13.09	90.2	235
XI	1.4 : 1.0	35.88	39.36	12.15	14	45	12.96	90.3	238
XII	1.4 : 1.0	37.08	40.67	12.57	14.	60	13.41	90.4	236
XIII	1.4 : 1.0	37.19	40.75	12.59	13.	60	13.40	90.1	236
XIV	1.4 : 1.0	35.73	39.19	12.13	17	90	12.41	86.8	235
XV	1.5 : 1.0	39.95	39.43	13.04	13	45.	13.05	90.7	236
XVI	1.5 : 1.0	37.08	40.66	13.45	12	60	13.50	91.0	238
XVII	1.6: 1.0	36.57	40.31	14.22	14	45	13.46	92.0	238
XVIII	1.7: 1.0	36.59	40.13	15.04	13	45	13.47	92.0	238
XIX	1.8 : 1.0	35.92	39.40	15.63	14	.45	13.11	91.2	238

* With decomposition

General Observation

In all nitrations some slight frothing occurred with nitration mixture passing through a pale green colouration to very pale yellow; nitration mixture was slightly exothermic in behaviour. This was observed most markedly in the more prolonged nitration. Reaction mixtures possessed an odour of acetaldehyde and i n one instance it was thought that a trace of ethyl nitrate was also present.

In experiments using high nitric acid ratios some frothing occurred on drowning. Waste acid in these cases was somewhat yellow and some slight degradation seemed to occur in the liquor.

Melting Points of crude nitroguanidine

Melting points of all crude product were determined using a Gallenkamp electrical heating melting point apparatus. The specimen was inserted at about 200°C. and the rate of heating maintained constant for each sample.

All samples of crude nitroguanidine showed melting points in the range 235-238°C., with decomposition.

Purification of crude nitroguanidine

(i) 12.94 g. crude nitroguanidine (Exp. XVIII, Table X) was dissolved in 250 ml. water, in the warm. No apparent degradation was observed and the solution was water white and clear. The solution was allowed to cool and stand overnight. The crystalline product was collected; the filtrate

was used for transferring last traces of solid from beaker on to the filter. The product was dried, to constant weight, overnight at 100°C.

Temperature of filtrate, 22°C.
Weight of recovered product, 11.65 g.
Solubility of nitroguanidine at 20°C., 0.260g. in 100 c.c. H_2O.
Solubility increment, 0.23 g/°C. in range 20 to 40°C.
Solubility correction for 250 cc. solution = 0.765g.
Total weight of recoveredproduct, correct, 12.41g.
Loss on recrystallisation, 0.525g.
≡ 4.057 per cent.

(ii) 12.42 g. crude nitroguanidine (Exp. V, Table X), was dissolved in 339 ml. H_2O in the warm. Solution was cooled to 25°C and allowed to stand, with occasional stirring, for 1 hour. The crystalline product was collected as in (i) and dried at 100°C. It was weighed after 4 and 8 hours and showed constant weight.

Temperature of filtrate, 25°C.
Weight of recovered product 10.79g.
Solubility correction, 1.272g.
Total weight of recovered product, corrected, 12.062.
Loss on recrystallisation, 0.36g.
≡ 2.898 per cent.

Purity of recrystallised nitroguanidine

(i) Batches 6, 13, 14 and 19 (Table X) were dissolved in 1200 ml. hot water to give a clear solution. The solution was allowed to cool slowly at room temperature. The crystalline product was collected.

A sample was submitted to the specification tests for service grade material.

The sample satisfied all tests.

(ii) The Infra Red Spectra, of a sample of recrystallised nitroguanidine prepared from urea and a sample of recrystallised nitroguanidine prepared from guanidine nitrate, were compared under the same conditions. The spectra were indentical indicating that both samples were of strictly comparable purity.

F. Analysis of Waste Acids from Nitration Experiments

Waste acids from Nitrations XI and XIII Table X were subjected to a number of analyses to determine the approximate composition.

The nitroguanidine/waste acid mixture after drowning was weighed complete and the total weight of waste acid obtained by subtracting the weight of any nitroguanidine recovered.

After filtering off crude nitroguanidine the main bulk of waste acid was collected, weighed and made up to 250 ml. in water. Aliquot portions of this solution were used for the various analyses. All results were calculated on the basis of the entire material from Gu HSO_4, Batch IV, being nitrated under the conditions of the experiment (i.e. material from 4 GRM. MOLES of urea.)

The following determinations were carried out.

(1) Total Acidity

5 ml. portions of the acid solution were titrated against N/1 sodium hydroxide using methyl red indicator. Total acidity is expressed as sulphuric acid.

(2) Total Sulphate

25 ml. of the acid solution was diluted with water and made up to 200 ml. Portions, 10 ml., of the resulting solution were analysed for total sulphate by the normal barium sulphate method. Total sulphate ion is expressed as sulphuric acid.

(3) Free Sulphuric Acid

5 ml. portions of the acid were diluted with water and evaporated to small bulk on the steam bath to remove volatile acids; dilution with water and evaporation was repeated three times; remaining sulphuric acid was titrated against N/1 sodium hydroxide usihg methyl red indicator.

(4) Total Nitric Acid

Estimated by colourimetric method of Murty and Gopalarov (12) using 1 - naphthol - 5- sulphonic acid. Nitric acid is expressed as nitramine group, $-N.NO_2$.

(5) Free Nitric Acid

The normal nitron procedure indicated only a trace of free nitric acid.

(6) Amine Salts

(a) 5 ml. of the acid solution was added to 50 ml. N/1 sodium hydroxide and the solution boiled for 10 mins. The solution was then cooled and titrated against N/1 sulphuric acid using methyl red indiciator.

Alkali consumption in excess of that due to acidity already determined was calculated as ammonium sulphate on the basis of the equation.

$$(NH_4)_2 SO_4 + 2 NaOH = 2 NH_3 + Na_2 SO_4 + 2H_2O.$$

(b) Using the method of Grisson (6) 5 ml. of the acid solution was neutralised to methyl red with N/10 sodium hydroxide solution; 5 ml. 40% formalin + 15 ml. water, previously neutralised to phenolphthaleim was added and the solution allowed to stand 5 mins. Acidity which developed was titrated against N/10 sodium hydroxide to the phenolphthalein end point.

1 ml. N/10 sodium hydroxide = 0.0066g. $(NH_4)_2 SO_4$.

(7) Reducing Material

10 ml. of the acid solution was added to 25 ml. N/10 potassium permanganate and the solution allowed to stand 5 mins. Excess potassium iodide solution was then added and the liberated iodine titrated against N/10 sodium thiosulphate. Reducing material was calculated as nitrous acid on the basis:

Nitrous acid = $(25.0 - \text{ml. } Na_2S_2O_3) \times 0.00235$ g.

(8) Total Nitrogen

10 ml. of the acid solution pippetted into a Kjeldahl digestion flask. and evaporated to small bulk. The residue was analysed for total nitrogen by the normal Kjeldahl procedure.

(9) Weak Acids

5 ml. of the acid solution was added to 25 ml. N/1 Sodium hydroxide and the resulting solution titrated against N/1 sulphuric acid, using phenolphthalein and methyl red indicators.

The difference in titres due to the presence of weak acids in the original acid solution was calculated as carbon dioxide.

Analytical data for both samples of acid are summarised in Table XI.

Table XI

Total weight of waste acid, Exp. XI (Table X) 6997 g.

" " " " " Exp. XIII (Table X) 6673 g.

Composition	Waste Acid, Exp. XI.		Waste Acid, Exp. XIII.	
	g.	%	g.	%
Total acidity, as H_2SO_4	1226	17.52	1220	18.28
Total SO_4 ion, as H_2SO_4.	1273	18.22	1254	18.79
Free H_2SO_4	1181	16.89	1176	17.63
Free HNO_3	nil	nil	nil	nil
Fixed HNO_3, as - $N.NO_2$	46.0	0.66	53.9	0.81
Bases as $(NH_4)_2SO_4$ (a)	78.9	1.13	79.0	1.84
Bases as $(NH_4)_2SO_4$ (b)	71.4	1.02	71.5	1.07
Potential N as $(NH_4)_2SO_4$	193.6	2.77	193.6	2.90
Total N	41.11	0.59	41.1	0.61
Weak acid as CO_2	5.9	0.08	5.8	0.09
Reducing material as HNO_2	4.3	0.06	5.1	0.08
Water (approx.) calculated	5408	77.29	5164	77.38

Analyses of Gu. HSO_4, Batch IV

In conjunction with the analyses made on waste acids from nitration of Cu.HSO_4, Batch IV, the following additional analyses were made on this material. Quantities were calculated for the whole batch (4 gram. mol. urea).

Amine salts

Determined by the method of Grisson (6). Total amine salts as $(NH_4)_2 SO_4$, 56.5 g.

Total Nitrogen

Determinedby the Kjeldahl Method.

Total Nitrogen present, 160.1 g.

G. Flowsheet Data and Materials Balance

The collected experimental data obtained in Preparation IV, Section 26 and Experiment 13, Tables X and XI (this Section) furnish a typical flowsheet and materials balance for a process for the production of nitroguanidine (picrite) from urea. The collected data are tabulated below:

[redacted]

Flowsheet Data

	Grms.	Parts/part pure picrite
Raw Materials (Theoretical quantities)		
Ethylene, used	224.0	0.853
Ethyl Alcohol, used	368.0	1.402
Sulphuric Acid, used	392.0	1.494
Water, produced	144.0	0.549
Alkylation Stage		
Urea, used	240.0	0.914
Ethyl Sulphate, used	616.0	2.347
U[1] / Et \ SO_4 + I, product	856.0	3.261
Amination Stage		
Ammonia (theory)	49.5	0.189
Ammonia (used)	66.0	0.251
(Exit)	20.4	0.078
Gu / Et \ SO_4 + I, product	772.1	2.942
Ethyl Alcohol, recovered	149.9	0.571
Hydrolysis Stage		
Water, used	155.4	0.592
Sulphuric Acid (100%), used	76.7	0.292
Ethyl Alcohol, recovered	159.7	0.609
Water, recovered	84.4	0.322
Gu HSO_4 + I, product	757.1	2.885
Analysis - Bases as $(NH_4)_2SO_4$	56.4	0.215
Guanidine	171.9	0.655
Sulphuric acid free	235.7	0.898
Sulphuric acid as Gu_2SO_4	142.8	0.544
Potential N_2 as $(NH_4)_2SO_4$	754.8	2.876
Nitration Stage		
Sulphuric Acid, used	826.9	3.151
Nitric acid, used	254.5	0.970
Water, used	18.0	0.069
Picrite (crude), product	273.8	1.043
Picrite (pure), product)	262.5	1.000
Water, used for dilution	5090.0	19.39
Waste Acid, recovered	6673.0	25.420
Analysis - Total Acid as H_2SO_4	1220.0	4.648
Total SO_4 ion as H_2SO_4	1254.0	4.777
Free H_2SO_4	1176.0	4.481
Free HNO_3	nil	nil
Fixed HNO_3 as $-N.NO_2$	53.9	0.205
Bases as $(NH_4)_2SO_4$	71.5	0.272
Potential N_2 as $(NH_4)_2SO_4$	193.6	0.738
Weak acid as CO_2	5.8	0.022
Reducing material as HNO_2	5.1	0.019
Water, calculated	5164.0	19.67

Flowsheet Data (contd.)

	Grms.	Parts/part pure picrite
Concentrated Waste acid (Theoretical quantities)		
Sulphuric Acid, recovered	1110.0	4.229
Ammonium Sulphate, recovered	193.6	0.738

$$U' \equiv \left[C \begin{matrix} \diagup NH_2 \\ - OC_2H_5 \\ \diagdown NH_2 \end{matrix} \right]^+ ; \quad Gu \equiv \left[C \begin{matrix} \diagup NH_2 \\ - NH_2 \\ \diagdown NH_2 \end{matrix} \right]^+ ; \quad I = \text{other products.}$$

Recovery of C_2H_5 groups, as C_2H_5OH, from $(C_2H_5)_2SO_4 \equiv 84$ per cent.
Recovery of SO_4 radical, as active H_2SO_4, from $(C_2H_5)_2SO_4 \equiv 77$ per cent.

Materials Balance

	Parts/part pure picrite
H_2SO_4 for Et_2SO_4	1.494
H_2SO_4 for Hydrolysis	0.292
H_2SO_4 for Nitration	3.151
Therefore total input of H_2SO_4	4.937
H_2SO_4 recovered in Waste Acid	4.229
Therefore Consumption of H_2SO_4	0.708
Et OH for Et_2SO_4	1.402
Et OH recovered from amination	0.571)
Et OH recovered from hydrolysis	0.609)
Total EtOH recovered	1.180
Therefore Consumption of EtOH	0.222
NH_3 consumed at amination	0.251
NH_3 required for urea	0.518
Therefore Consumption of NH_3	0.769
CO_2 required for urea	0.671
Therefore Consumption of CO_2	0.671
Consumption of HNO_3	0.970

28. Solubility Data

These were determined at an early stage in the work and are now recorded.

(i) The solublities of Sodium and Potassium Ethyl Sulphates in Water at 20°C.

Saturated aqueous solutions of the salts were prepared at 20°C. Aliquot portions of the solutions were pipetted into weighed dishes, weighed, evaporated to dryness and the residue weighed.

The data obtained are given below.

	100 ml. Saturated soln. contain. grms.	100 ml. Water dissolve grms.
Sodium Ethyl Sulphate	76.3	135.8
Potassium Ethyl Sulphate	87.3	177.8

(ii) <u>The solubility of Guanidine Nitrate in a saturated aqueous Sodium Ethyl Sulphate Solution at 20°C.</u>

A portion of saturated sodium ethyl sulphate solution was saturated at 20°C. with guanidine nitrate. An aliquot portion of the solution was pipetted into a weighed dish, weighed, evaporated to dryness and the residue weighed. The residue was further analysed for guanidine and the composition of the solution calculated.

	100 ml. saturated soln. at 20°C. contain.	100 ml. water at 20 °C. dissolve.
Guanidine Nitrate	21.1 g.	45.8 g.
Sodium Ethyl Sulphate	66.2 g.	143.9 g.

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1 Jul 83

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